

SEDIMENTARY PETROGRAPHY

*With Special Reference to Petrographic Methods of
Correlation of Strata, Petroleum Technology
and other Economic Applications of Geology*

VOLUME I

METHODS IN SEDIMENTARY PETROGRAPHY

by

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CHAPTER I

INTRODUCTION TO THE STUDY OF SEDIMENTARY ROCKS

DEFINITIONS AND RETROSPECT

SEDIMENTARY rocks include all consolidated and incoherent sediments composing the earth's crust, irrespective of their mode of origin, other than those rocks formed directly by igneous agency; they thus embrace rocks of mechanical, organic and chemical origins and characteristics¹.

The petrology of sedimentary rocks implies their comprehensive study by relevant chemical, geological and physical methods, both in the field and in the laboratory, leading to an understanding of their natural history, in so far as such study may guide its interpretation. This phase of the science is, in fact, complementary to the much wider field of traditional stratigraphy—'sedimentary geology' (as it was sometimes termed)—or the more popular word *sedimentology* as in recent years it has come to be known in international parlance; this means, essentially, studies into modes of formation and distribution of sedimentary rocks of whatever nature and characteristics, wherever developed throughout the world.

'Le domaine de la sédimentologie est notablement plus vaste que celui de la pétrographie sédimentaire. Le premier est à l'échelle du bassin, le second à celle de l'échantillon de roche. A vrai dire, la

¹ Pyroclastic rocks, *i.e.* fragmental products of explosive volcanic action, when deposited under water, frequently become admixed with ordinary sedimentary detritus; they may thus exhibit stratification and sometimes contain fossils. These rocks, however, constitute a special case, falling by affinities with volcanic rocks more naturally within the domain of igneous petrology; their consideration is consequently omitted from this book.

*pétrographie n'est qu'une partie de la sédimentologie, son aspect technique de laboratoire. Il y a donc deux grandes tendances dans cette science: l'une vers le terrain, l'autre vers le laboratoire. Des progrès très notables ont été accomplis dans ces deux directions, ces dernières années*¹.

Needless to say at outset, as the title of this book implies, emphasis is herein laid on practical laboratory investigations of sediments; on all modern techniques designed to elucidate the innumerable problems they present, both academic and economic, from whatever specialized technical knowledge such techniques may stem.

Sedimentary petrography may be defined as the systematic description of sediments, implying both their lithology and mineralogy and, by interpretation of these functions in a wider sense, their genesis. Lithology means determination of rock characteristics in the mass *in situ* as well as by megascopic observations of representative hand-specimens in the laboratory. Mineralogy of sediments plays a vital role in this petrography; all modern methods now available in examination and diagnosis of many thousands of species known in the mineral kingdom are today at the disposal of the sedimentary petrographer, a vastly different state of things to those obtaining half a century ago when sedimentary rocks as such were taken for granted, their intensive study, compared with their igneous counterparts, sadly neglected. A curious apathy to studying sediments for their own sake pervaded spheres of geological learning in those days; a consequent dearth of fundamental information, certainly on British sedimentary rocks, was only really corrected as a direct result of internal economic exigencies of the first world war. Prior to this, contributions to our knowledge of these rocks were, if occasionally outstanding, none the less sporadic. In the teaching world, sediments were fortunate if they received brief treatment and speedy dismissal at closing stages of full courses in igneous petrology. In the realm of stratigraphy, it was field-relationships and fossils that gave individuality to these rocks, not their inherent composition and provenance. So it was generally in petrological research, where for every one pioneer in studies of sediments, igneous petrology could claim a score. All that has since altered; work of more than four decades, both in Britain and overseas, has brought this branch of natural science into the forefront of both philosophic and economic geological thought, wherever sediments are involved.

Looking back, it is interesting to speculate to what extent the 'heavy mineral' cult was responsible for awakening long-delayed interest in sediments, but herein may lie a claim with some foundation. Constant repetition of sedimentary rock-types as studied in the field, or in the laboratory in thin section, might perhaps be an excuse

for general lack of interest in them; but an ever-changing galaxy of diverse mineral grains, once their broader significance was appreciated, could not do other than prove stimulative.

On the purely academic side, the tendency was at first towards study of the subject for its own sake, with little or no regard for its broader possibilities; sampling a particular sediment, segregation of its 'heavier' and more stable constituents and their ultimate mineralogical analysis, formed a welcome change from routine investigation of thin sections of consolidated rocks, one followed mainly because it was, indeed, a new departure in experimental petrology. This narrowness of treatment, however, was destined to be rapidly transgressed, as investigators became more and more imbued with broader potentialities of the subject; it was soon realized to what extent certain fundamental problems in stratigraphical geology were susceptible to resolution along these lines. Questions concerning genesis of a sediment, involving not only concepts of provenance but also of mode of transport and deposition, nature of environmental and climatic conditions at the time of its formation—together with such pertinent aid afforded by the data to palaeogeographical restoration—all eventually came to be embraced by systematic petrographical examination of sedimentary deposits thus intensively investigated. It is not difficult, therefore, to appreciate reasons underlying the rapid and in some respects remarkable evolution which occurred from the early 'twenties of a technique offering so many far-reaching possibilities.

Apart from these more academic motives, the 1914-18 war period saw an impetus to critical research on sedimentary rocks such as had never before been attempted on a large scale in this country, nor at the time elsewhere for that matter. Among other things the emergency created urgent necessity to utilize national resources of indigenous sediments of one kind or another, of potential industrial value, to replace former imported foreign supplies then denied by wartime exigencies. This work became not only fundamental from an economic standpoint, but both then and subsequently exerted considerable influence in establishing this science on a firm and modernized basis. The projects involved such materials as sands suitable for glass-making, foundry work and other purposes; new investigations into such sedimentary rock-types as ganister, silica rock, fireclay, dolomite for refractories; ball and china clays for ceramics and other commodities; oil-shale, lignite, cannel-coal as fuel resources; bedded iron ores for the steel industry; rock-salt deposits for heavy chemical industries and domestic needs, etc. Thus was accumulated a mass of hitherto unpublished data, both chemical and petrographical, which has since proved to be an invaluable guide in later researches on these and other sediment resources in Britain.

In another direction sediments were being attacked from an entirely different angle, especially overseas. The rapid development of petroleum geology during this same period and the complex problems besetting subsurface identification and correlation of frequently *unfossiliferous* strata penetrated by the drill, led to consideration of possibilities of petrographic methods in this connexion. In Trinidad in 1915 and subsequently, V. C. Illing demonstrated the great value attaching to a detailed petrological study of the highly disturbed oil-bearing strata in the southern part of that island. His recognition of successive groups of sediments characterized by exclusive heavy mineral assemblages, constituted a new weapon of attack on problems of differentiation and correlation of strata which had previously defied solution. Thus was laid the foundation of this particular application of petrographic methods to stratigraphical analysis—one destined to aid substantially investigations of oilfield sediments in other countries besides Trinidad, as well as sedimentary deposits at home and abroad.

INTERNATIONAL RESEARCH ON SEDIMENTARY ROCKS

The following survey of 'milestones' in the progress of building-up this science as we know it today, covers a span of nearly eighty years, from late nineteenth century until present time. This review is necessarily brief; many distinguished names throughout the records of this period are inevitably omitted, to which fact the bibliography at the end of Vol. II bears eloquent testimony. What is attempted here is to provide the reader, particularly the student-newcomer to this subject, with sufficient background to appreciate the essential steps by which sedimentary petrography has evolved to its present status in both pure and applied geology, in preparation for contemporary studies and future developments in this subject, the primary purpose of this book to demonstrate. The arrangement adopted is conveniently that of the individual countries chiefly concerned in this history, beginning with the United Kingdom.

THE UNITED KINGDOM (PRE-1920)

BRITISH pioneer work on sedimentary rocks may be said to date from the time when H. C. Sorby first described his work on *The Structure and Origin of Limestones* (1879) and on *The Structure and Origin of Non-Calcareous Stratified Rocks* (1880)¹, in two communications which undoubtedly laid the foundations of the technique of study of sedimentary, as distinct from igneous, types. Admittedly other workers before him, both in this country and overseas, contributed descriptions of sediments

¹ See Bibliography, Vol. II, for these and other references to authors mentioned in ensuing paragraphs.

in which some measure of mineralogy was uppermost; but the literature has to be critically searched for previous efforts which have 'lived' to be still in any sense terms of reference.

A frequently quoted first paper in the realm of heavy mineral investigation, for instance, is that of A. Dick, who recorded his observations *inter alia* on the Bagshot Sands of Hampstead, London, in 1887; this brief contribution to *Nature* apparently did not excite the imagination it might have been expected to do among contemporary petrologists; but it has become a minor classic of its kind in the annals of sedimentary petrography. In the same year, a paper by J. J. H. Teall described the occurrence of rutile needles in certain clays and showed that the author of *British Petrography* (1888) was fully alive to possibilities of intensive investigation of constituents of the finer grained sediments, even though his *magnum opus*, save for one illustration, contained nothing at all on sedimentary rocks *per se*.

W. M. Hutchings' essays on detrital minerals of clays and slates (1890, 1894) revealed still further what could be done by painstaking analysis of fine-grained sediments; these papers are still often remembered in contemporary thoughts. Then came W. Mackie; his published work, from an early account of *Sands and Sandstones of Eastern Moray* (1896), was followed in 1897 by consideration of the mechanism of rounding of sand grains (a fitting prelude to modern research on shape and size of incoherent rock-particles).

The year 1900 saw publication of T. G. Bonney's researches into *Bunter Pebble Beds of the Midlands*, in which he dealt with their petrography, mode of transport and possible source of origin. Though dealing essentially with pebbles and boulders, the principles he demonstrated clearly established a basis of parallel reasoning in the natural history of finer material. Shortly afterwards (1902) there appeared an outstanding paper by H. H. Thomas on *The Mineralogical Constitution of the Finer Material of the Bunter Pebble Bed in the West of England*, a model of mineralogical accuracy and palaeogeographical vision which revolutionized contemporary work on sedimentary deposits of this kind. This paper was followed in 1909 by a similar contribution on *The Petrography of the New Red Sandstone in the West of England*, in which that author again made evident the vital importance of precision in mineral grain determination, the significance of provenance and the stratigraphical value of these inorganic indices of past events. Many publications by others of a similar character have since appeared, but each inevitably bears tacit, if not actual, acknowledgment of the teachings of that great petrographer.

Attention may be drawn at this stage to two essays of outstanding merit which can still be read with advantage by all students of sedimentary petrography in its broadest applications; both are presidential addresses delivered to the Geological Society of London, one by J. E. Marr (1905) on *Classification of Sediments*, the other by W. W. Watts (1911) on *Geology as Geographical Evolution*. In the former paper analogy was drawn between meteorograms, as recording meteorological variations, and 'geograms', a word used by J. E. Marr in place of the

expression 'Geological Column' and connoting principally variations in lithology and in organic assemblages that could be traced in a deposit, if a column obtainable from boring right through it were laid flat and studied from one end to the other. Although purely a hypothetical conception, the 'geogram' was the ideal to which, he implied, all petrographic investigations should tend even though tracings are broken or discordant, as they are bound to be, the evidence could be none the less valuable and suggestive. W. W. Watts enlarged this conception in the following words: 'In order to obtain what Dr. Marr has called the "geogram" of a formation in its greatest perfection, we require to know the entire extent of its variations, not only along its outcrop, but in that part which is hidden from sight; and we ought to be in a position to infer the probable variations in that almost equally important part which has been destroyed by denudation'.

The few years preceding 1914-18 were not conspicuous for prolific publication on sediments, but some research was none the less in train; H. H. Thomas continued his descriptive work on varied West of England deposits; T. Crook dealt with technique (1908-09) and also gave the first systematic account of the then-known commoner detrital minerals in an appendix to F. H. Hatch's *Petrology of Sedimentary Rocks* (1913); G. M. Davies published (1912) the first of a series of useful papers on the mineralogy of different sediments in London and the home counties; R. H. Rastall devoted much attention to technique and mineralogy of Cambridgeshire sands and gravels (1913).

Then came the war period (1914-18) when research was intensified, although essentially economic in bias, as previously mentioned (p. 21). To appreciate advances made at this time, both in technique and outlook in this subject, the reader is referred to a suggestive article on *The Application of Petrological and Quantitative Methods to Stratigraphy* by P. G. H. Boswell (1916), which in fact gave a significant pointer to the methods whereby J. E. Marr's 'geogram' might best be attained; this essay co-ordinates facts and gives constructive criticism of hypotheses then current.

THE UNITED KINGDOM (1920-1940)

With the post-war (1914-18) period came a flood-tide of enthusiasm for sedimentary petrology in this country and both in teaching and research, much energy was devoted to the subject in geological departments of universities, technical colleges and other centres of learning; the number of workers in this field thus rapidly increased. About this time some original work on Yorkshire sediments was accomplished, culminating in an inspiring account of Millstone Grit by A. Gilligan (1920)—a pattern for similar investigations on pebble-bearing sandstones and their origin, to be followed by investigators in subsequent essays on similar, complicated deposits.

The author's own researches on correlation of isolated Tertiary deposits in Western Cornwall (1922); on certain Wealden sediments in south-east England (1922-25); and on innumerable well-samples from

oilfields visited in the United States (1923) and Middle East (1927–28), aided development of technique of differentiation and correlation of sediments, based on assessments of 'heavy' mineral suites, and served to sustain both validity and value of these petrographic methods as applied to elucidation of stratigraphical and especially subsurface structural problems.

A further application of the subject to alluvial mining was described by the author in 1923 and subsequently became the theme of a separate textbook on *Alluvial Prospecting* in conjunction with C. Raeburn (1927). This phase of 'Sedimentary Mineralogy', as it was at the time aptly termed by A. Holmes, is both in principle and practice but a logical outcome of comprehensive study of sediments, whether recent or ancient; the particular technique implied has since influenced developments of alluvial mineral deposits in many different parts of the world. Quite apart from an economic bearing, investigation of alluvial 'heavy' minerals is of the greatest possible value—incidentally a most fascinating pursuit—in all problems of detrital mineralogy.

In another direction intensive research was proceeding on accessory minerals *inter alia* in igneous rocks, leading to some highly original dissertations by A. Brammall and H. F. Harwood on Dartmoor Granite (1923), giving results of detailed geochemical and petrological observations profoundly affecting conceptions of provenance and significance of sedimentary rock minerals, quite apart from the direct influence of this work in the domain of igneous petrology. These authors firmly established a technique (initiated on a smaller scale by R. H. Rastall and W. H. Wilcockson (1917) in investigation of certain Lake District granites), involving isolation and intensive study of accessory minerals in igneous rocks, since become the pattern of a large volume of similar work both at home and abroad. A. Brammall followed this up with another classic paper on Dartmoor Detritals (1928), a pertinent study in provenance of sediments, creating a high standard of precedence for this philosophical phase of the subject.

Other landmarks between the 'twenties and early 'thirties were the work of S. W. Wooldridge on the *Bagshot Beds of Essex* (1924) and on *The Pliocene History of the London Basin* (1927), both distinctive for originality of thought and interpretation in deciphering the natural history of the rocks of this part of England; equally W. F. Fleet's minutely detailed contributions to our knowledge of Palaeozoic sediments in the Midlands (1923–33); again, F. Smithson's descriptive work on accessory minerals of certain Irish granites (1928), his careful enquiries and deductions on frequency estimations of heavy mineral suites (1930) and his later work on *The Triassic Sandstones of Yorkshire and Durham* (1931), are each noteworthy contributions to the subject. I. S. Double (1924–31) contributed various papers on petrography of sediments, characterized by careful attention to detail of mineral constitution. Outstanding, too, as breaking new ground, were researches carried out by A. W. Groves (1931) on the influence of unroofing of Dartmoor granite in contributing to sedimentary deposits over a large area of southern England, a fitting corollary to the pioneer work of A.

Brammall and H. F. Harwood *supra*. Petrographic methods were vigorously employed by J. D. Solomon in studies of glacial deposits of East Anglia (1932), thus ensuring this technique an established place in unravelling complex problems of Quaternary geology.

It was during these two decades too, especially early 'thirties, that another outlet for resourceful students of sedimentary petrography became abundantly manifest. Co-investigators in border-sciences concerned with clays and clay minerals, *e.g.* agriculture, ceramics, oil-well drilling muds, refractories, soil-science etc., had proclaimed their faith in the new techniques then available in studies of finely divided mineral matter, in ultimate particle size, beyond diagnostic range of the ordinary petrological microscope. The pioneer work of W. L. Bragg and development of the technique of X-ray diffraction analysis, forged a weapon of attack on clay mineralogy of which quick advantage was taken both in this country and abroad, with the result that researches into clay complexes were revitalized and expanded with extraordinary rapidity. Today clay technology can claim to be a science in its own right; much that was little understood in the early years, especially with regard to characteristic physical properties of clay materials, *e.g.* plasticity and behaviour under thermal stress, has now been revealed by identification of distinctive minerals involved and especially an understanding of their atomic structures. The subject is dealt with in some detail by our specialist contributor, D. Carroll (Vol. II, Ch. III).

Foremost among contributors to British literature on this subject, during this 1920-1940 period, should be mentioned G. W. Robinson (1922-37), whose work on clays and soils is well known, his text-book on *Soils* (1936) still widely read; E. F. Newton's petrographic researches on English Fuller's Earth deposits (1934-37); C. E. Marshall, to whom students are indebted for a number of valuable papers on clay minerals, lattice structure of clays, etc., of international repute (1935 and subsequently, *q.v.*).

Yet another vista was unveiled around this time, a little narrow then, perhaps, but destined to offer far-reaching opportunities for more mathematically minded students of sedimentary petrology. It has on more than one occasion in the past been said that geology is an inexact science, probably with some truth. In this particular branch of geology, mere qualitative assessment *per se* of relative frequencies of 'heavy' minerals in a given sediment-sample, for instance, gradually came to be frowned upon by those who sought to introduce some degree of precision into such estimates, with justification. What more natural than to invoke aid of proven statistical methods for such purpose or, for that matter, in other studies of sedimentary rocks, *e.g.* orderly outcrop-sampling? In this country, possibilities of this specialized approach were unfolded during the

latter years of the period under review. The subject is undeniably complex; it has grown more so; in its modern trends in this petrology, it is lucidly explained by our specialist contributor J. C. Griffiths (Ch. XVI).

To F. Smithson (1939) is due credit as being one of the original exponents in the United Kingdom at that time of statistical methods applied to sedimentary petrography, graphical, cartographical, etc. Other investigators in the United States had previously attacked similar problems from this angle (*q.v.*, p. 28). Nevertheless, introduction of statistical maxims in the realm of descriptive work on sedimentary deposits was then viewed with some trepidation by those for whom quantitative methods, applied to these materials, immediately conjured up visions of classifications and calculations emulating the famous 'C.I.P.W.' system for igneous rocks, established in the early years of the present century¹. None the less, these applications had definitely come to stay, as subsequent events have confirmed beyond doubt.

THE UNITED KINGDOM (1941 ONWARDS)

Despite severe ordeals due to enemy action suffered by some of our largest cities, involving universities, technical colleges and other seats of learning, looking back, the second world war (1939–1945) did not impede academic or economic progress in this science as much as might otherwise have been reasonably anticipated. There was, in fact, quite a steady flow of original work during this period, even though publication was retarded; also a concomitant intensification of industrial research concerned with indigenous sedimentary raw materials ensued, much the same as during the 1914–18 episode. Such lag as happened was soon made up in immediate post-war years; now, nearly two decades of continuous and expanding research into fundamentals of this greatly ramified subject discloses not the slightest sign of abatement of its disciplines; rather, if anything, an acceleration of pace in the many avenues of investigation still open to *prima facie* research. Again it is the finer sediments, clays, still tending to advance to the fore-front of contemporary investigations, perhaps for far more subtle reasons than is casually apparent from research into, say, their intimate atomic make-up.

The borderland between this and fundamental biological concepts is becoming less clearly delineated; there already exists a fascinating glimpse into the not so far-distant future when that science may come to claim a most unexpected handmaiden from geology itself; when stratigraphy will at long last acknowledge the debt due to sedimentary petrology as well as to palaeontology, in its fuller and richer interpretation.

¹ W. Cross, J. P. Iddings, L. V. Pirsson and H. S. Washington, *Quantitative Classification of Igneous Rocks* (Univ. of Chicago Press, Chicago), 1903.

A review of outstanding contributions to this science from 1941 to present time, regarded internationally, reveals unquestioned accents on (a) precision in description of sedimentary rocks, (b) quantitative evaluation of their fundamental mineralogical and physical characteristics, and (c) expansion and development of all modern instrumental and analytical techniques geared to solution of the still many unsolved problems in constitution and behaviour of these 'aggregates of mineral particles'. Modern literature discloses a healthy trend in breaking new ground; in departure from merely cataloguing observations into a philosophical appraisal of what role sedimentary rocks really have played in the past and contemporary natural sediments are now assuming, in the history of the earth as it more rapidly unfolds today.

In all this evolutionary thought, this country has certainly not lagged behind, as the following brief résumé of work of selected authors demonstrates. Again, it is emphasized that in the limited space available here, the intention is to pin-point projects which, in the author's opinion, have profoundly influenced or in other ways materially aided advancement of this science. This chronicle is not a bibliography, to which the reader is necessarily referred for a more detailed cross-section of events in this subject during the period under consideration (Vol. II). The procedure is by authors arranged alphabetically as far as practicable.

Researches of P. Allen on statistical aspects of the subject (1944-47) served to underline the growing need for consolidating the quantitative elements in studies of sedimentary rocks, already urged by F. Smithson (1939). His provocative paper on *Wealden Petrology: The Top Ashdown Pebble Bed and the Top Ashdown Sandstone*, although seemingly parochial, is, in fact, a most stimulating blend of precise, detailed description of these well-known beds, statistical evaluation of particle-size and frequency variations, and logical interpretation of data thus elucidated, with implications in principle reaching far beyond the actual subject of this enquiry itself. P. G. H. Boswell (1948) directed attention to thixotropic behaviour of sediments which, excepting coarse clean sands and gravels, are potentially capable of assuming the thixotropic state (isothermal, reversible, gel-sol-gel transformation); thixotropic values for many British sediments were established and a lead given to their meaning in fundamental geological processes. He also discussed (1952) influences of clay mineralogy in studies of diagenesis of sediments. In an elaborate scheme of team-work research into pneumokoniosis (silicosis) in South Wales coalminers, sponsored by the Medical Research Council, A. Brammall and J. G. C. Leech (1943) carried out some original investigations on Coal Measure shales and sandstones primarily 'to determine whether the strata exposed at the coal-face in mines with a low incidence of pneumokoniosis differed petrologically from those exposed in mines with a high incidence'. The techniques involved, apart

¹ *Spec. Rep. Series 244, 2, Environmental Studies*, 1943, p. 125.

from conventional petrographic methods, were *inter alia* pH determinations on water extracts, base-exchange capacities of air-elutriated preparations from matrix matter, diethylamine precipitations of colloidal silica and alumina (solubility of minerals and mineral gels in aqueous diethylamine) of the finer constituents of clays and shales; potentialities of these novel methods of attack on these complex rocks and their bearing on studies in clay mineralogy are highly suggestive and of much consequence in similar investigations elsewhere.

The name of G. W. Brindley is instinctively linked with clay mineralogy, notably his studies of chamosite (1949), chamosite minerals (1951) and X-ray methods of determining orientation of micaceous minerals in clays and shales (1953); with K. Robinson, structure of kaolinite (1946) and X-ray studies of fireclays and shales (1946-48); with K. Robinson and D. M. C. MacEwan, elucidation of halloysite and meta-halloysite; with R. F. Youell, studies in ferrous and ferric chamosite. As editor of and contributor to *X-ray Identification and Crystal Structures of Clay Minerals* (1951), published by the Clay Minerals Group¹, Mineralogical Society, London, he has provided students of this phase of the subject with an invaluable book of reference.

In contemporary studies of detrital radio-active minerals, C. F. Davidson and M. E. Cosgrove, by means of radiometric and mineralogical examination of pitchblende (uraninite)—shore-deposits in Cornwall (1955), effectively demonstrated an unexpected imperistence of this mineral, once released from parent-rock; this is a significant pointer to what may happen elsewhere when radio-active ores of this nature are exposed to denudation e.g. alluvial deposits. The technique they employed has decided possibilities in tracing not only movement of radio-active species under subaerial conditions, but also their provenance.

Ever-increasing demand for new resources of ganister and silica rock for refractories has, in latter years, led to more intensive field-work and given a collateral impetus to petrological analyses, not only of raw materials but equally of synthetic products. W. Davies (1948) urged that with progressive exhaustion of resources of high quality ganister in Britain, other quartzites and quartzitic sandstones would have to be utilized; his survey of British resources and of chief petrological types was a timely pointer what was to happen in future. On the laboratory side, G. R. Rigby's *Thin Section Mineralogy of Ceramic Materials* (1948, 2nd ed. 1953) has proved an invaluable contribution to this rapidly expanding subject.

In the instrumental sphere, A. T. J. Dollar described a useful refractive index comparator for the microscope (1948), also dichroscopes for microscope stage and ocular (1950). Developments in improved polarizing microscopes owe much to the skill of A. F. Hallimond (1946-47), later in conjunction with E. W. Taylor (1948-50), culminating in *Manual of the Polarizing Microscope* (2nd ed. 1953) by the first author, wherein the increasing utilization of polarized light, not only in petrology but in kindred sciences where optical physics play such an important

¹ Founded 1947.

part, is shown to be more than balanced by progressively new developments in design of relevant instrumental equipment.

The contributions of K. C. Dunham to petrography of Permo-Triassic sediments of Cumberland (1949) and Liassic Ironstones (1952); of L. Hawkes on discovery of jet coal in Kentish Chalk (1945), on erratics of Cambridge Greensand (1943) and in English Chalk (1951), are noteworthy. To M. H. Hey we are indebted for the British Museum index of mineral species and varieties (1950) of material assistance in studies of specific sedimentary rock minerals. D. M. C. MacEwan's work on clay minerals has considerably advanced our knowledge of this subject notably among other studies on the montmorillonite group (1944-46), on halloysite minerals (1947), X-ray analyses of clays (1949) and on an interesting derivative of biotite, the montmorillonoid 'Cardenite' (1954). The pioneer work of C. E. Marshall has already been referred to (p. 26) and his original and important contributions to the science are spread through many scientific journals to which further reference is made in the Overseas section of this chapter. G. Nagelschmidt is another indefatigable worker on clay minerals (1941), composition of air-borne dusts (1943) and soil colloids (1944); with others he investigated the chemistry and rheology of clay (1947); with D. Hicks, chemical and X-ray diffraction analyses of South Wales coal seams and mineral matter in coal (1943)¹.

The impact of road research on this subject is revealed in many official publications by the Road Research Laboratory on aggregates for bituminous mixtures, concrete, etc., and where sedimentary rocks particularly are involved the name of A. H. D. Markwick (1941-45) will be remembered for his essentially practical contributions, later with F. A. Shergold (1945) who, through all succeeding years, has continued these investigations and added much to our knowledge, especially of mechanical properties of natural crushed rock and gravel aggregates. Two publications of the R.R.L., one on *Soil Mechanics* (1952), the other on *Concrete Roads* (1955) are relevant and merit a special note here.

This chronicle of research into sedimentary rocks in the United Kingdom is fittingly concluded by reference once again to F. Smithson who, by his stimulating and versatile approaches to both theoretical and practical sides of the subject, continues to dispense new and valuable data, for instance, his discussion of alteration of detrital minerals (1941); on petrography of Jurassic rocks of Yorkshire (1942); on phase-contrast microscopy for minerals (1946-48); in studies of North Wales soils (1953); on the habit of pyrite in some sedimentary rocks (1956) and, with G. Brown, on some interesting occurrences of dickitic sandstones in North Wales and Northern England.

OVERSEAS

The prodigious expansion of research on sedimentary rocks in the principal countries in the world, especially since 1945, is attested by

¹ See footnote 1, p. 28.

the progressively swollen international literature of this subject with which, in fact, it is almost impossible for any one person today to keep pace. The reasons are no doubt partly academic, but it is more probable that the impetus has stemmed from an essential and universal economic drive for raw materials intimately associated with sediments such as coal, oil, bedded ores, alluvials and beach deposits (especially radioactive minerals) and, in some cases, water. In the dynamic search for petroleum everywhere today, wherever there appears the slightest possibility of a lucky strike, we still recognize that same urge which, between wars, was so pre-eminently responsible for the evolution of sedimentary petrology then and now to the high scientific status to which it has risen. One result of the international cachet achieved by this science, is release of a mass of information on sedimentary provinces in different parts of the world, which, in the early days, had remained buried (by order) in the archives of oil companies; this undoubtedly has materially assisted in expanding bibliographies of this subject culled from sources not only at home, but in greater measure from abroad.

It is a fact that at the 18th meeting of the International Geological Congress (London, 1948), no section of the programme was devoted exclusively to sedimentary petrology, but following this Congress a meeting of sedimentary petrologists drawn from several different countries, recorded their verdict for establishing a union or international organization of all sedimentary petrologists, wherever they might be working. That step, to the founding of the International Association of Sedimentology in 1949 was a comparatively short one; the value of ensuing proceedings of Congresses held under its aegis cannot be sufficiently stressed. Again, at the 3rd World Petroleum Congress (Hague, 1951), a resolution recommended that 'sedimentological' researches, especially in the search for oil, should be developed. Thus it has come about that far more important contributions to this science are available today from different countries (frequently published in English, French and German, as well as in the language of the country of origin) and to this extent the contemporary student is fortunate in being able to acquire a much more broad-minded picture of events in this domain of geology than were his predecessors.

The task of presenting a concise account of this international work within restricted space is by no means an easy one and there are of necessity many omissions from this survey. To enable the reader to track down more easily sources of information in the several countries concerned, a different treatment of this phase of the subject from that previously followed with the United Kingdom, and in former editions of this book, has here been adopted. The continents primarily, their countries, and so to certain authors, are

arranged alphabetically, as far as practicable. The selected publications are for the most part current and/or serial, rather than those which have dated, are obsolete or otherwise obtainable with difficulty; these are the best known and probably the most widely consulted by contemporary sedimentary petrologists in the international field; they should be found in libraries of learned societies, scientific establishments and institutions, technical colleges, universities, etc., covering geological science. At the outset, the author gladly acknowledges the great assistance obtained from that valuable little volume by B. Mason on *The Literature of Geology*¹ (with his permission) which the reader would do well to consult for more detailed bibliographical information.

AFRICA

GENERAL. The quarterly bulletins of the Overseas Geological Surveys (London, H.M. Stationery Office) are most valuable sources of information on progressive investigations into the geology and mineral resources of British Colonial and Dependent Territories (global), and contain much of current interest to students of sedimentary petrology (with bibliographies). F. Dixey and E. S. Willbourn contributed a paper on *The Geology of the British African Colonies* at the International Geological Congress (18th session, 1948), which should be noted.

ALGERIA. Of the official publications of the Geological Survey (Service de la Carte géologique de l'Algérie), Series 5 (Petrography) from 1937 onwards is relevant. Certain publications of the International Geological Congress (19th session, 1952) should also be consulted.

ANGOLA. The Serviços de Geologia e Minas at Luanda has published an official geological survey map of this Portuguese territory in connexion with which a paper by F. Mouta in the Report of the International Geological Congress (18th session, 1948) contains explanatory details.

CONGO (BELGIAN). The geological survey of the Belgian Congo (Service géologique du Congo Belge et du Ruanda Urundi) Leopoldville, issue bulletins (since 1945); also Annales du Muséum du Congo Belge, Sciences géologiques (since 1948) are published by Musée du Congo Belge, Teruven, Belgium and are relevant.

EGYPT. The name of W. F. Hume is well known in connexion with geological investigations in Egypt (1927–1937) and several reports of the Geological Survey of Egypt (since 1900) are available. Pioneer work by T. S. Bowman on the petrography of cretaceous oil-bearing beds at Hurgghada (correlation by means of heavy minerals) dates back to 1925 (published 1931), the first intensive study of sedimentary petrography in Egypt ever to be undertaken.

EQUATORIAL AFRICA (FRENCH). Bulletins of the Geological Survey (Direction des mines et de la géologie de l'Afrique Equatoriale Française, Brazzaville) have been available since 1943. M. Nickles contributed

¹ *Amer. Mus. Nat. Hist.*, 1953.

a general geological account of the country (and of the Cameroun) in the Report of International Geological Congress (18th session, 1948).

ETHIOPIA. Geological information on this country is restricted. G. Dainelli is the author of *Geologia dell' Africa orientale* (Reale Accademia d'Italia, Rome), 1943, which is probably the most useful work on the subject at present available.

FRENCH WEST AFRICA. The geological survey (Direction des Mines de l'Afrique Occidentale Française) at Dakar, publishes bulletins (since 1938) and annual reports (since 1946).

GHANA (GOLD COAST). The Geological Survey (Saltpond) publishes bulletins (since 1925), memoirs (since 1929) and annual reports (since 1913) which are the best available sources of information on sedimentary deposits in this country.

GUINEA (SPANISH). A publication entitled *Geologia y Geografia Fisica de la Guinea Continental Española*, by J. D. de Lizaur y Roldan (Madrid, 1945), gives general information on this colony (obtainable from Dirección General de Marruecos y Colonias, Madrid), while certain publications of the Instituto Geológico y Minero de España (Madrid) are also relevant.

KENYA. The Geological Survey (Nairobi) issue reports and annual reports (since 1933). S. M. Coles' *Outline of the Geology of Kenya* (Pitman, Nairobi), 1950 and W. Pulfrey's *Geology and Mineral Resources of Kenya* (Bull. Imp. Inst., 45, 1947, p. 277), should be consulted.

LIBYA. There is a short paper on the Geology of Libya by A. Desio (*Geol. Rundschau* 33, 1942, p. 415), but otherwise published information is restricted.

MADAGASCAR. The Geological Survey (Direction des Mines et de la Géologie, Tananarive) publishes *Annales géologiques du Service des Mines* (since 1931), and *Travaux du Bureau géologique* (since 1949). See also a modern paper by A. Lenoble in Report of International Geological Congress (18th session, 1948).

MOROCCO (FRENCH). The authority in this territory is Service géologique du Protectorat de la République Française au Maroc (Rabat) and the publications come under *Notes et Mémoires* (since 1927). The Report of the International Geological Congress (19th session, 1952), should be consulted.

MOZAMBIQUE. There is a Geological Survey in this country (Serviços de geologia e minas, Lourenço Marques) and periodical bulletins are available (since 1937) which include information on sedimentary rocks.

NIGERIA. Many valuable bulletins of the Geological Survey of Nigeria (Kaduna Junction) are available since 1921, also occasional papers (since 1925) and annual reports (since 1930).

NYASALAND. The Geological Survey of Nyasaland (Zomba) issue bulletins and annual reports (since 1923).

RHODESIA (NORTHERN). A summary of the geological features of this region is given by T. D. Guernsey (*Colonial Geol. Min. Resources*, 1, 1950, p. 121).

RHODESIA (SOUTHERN). The Geological Survey of Southern Rhodesia (Salisbury) publishes bulletins, reports and annual reports (since 1917) which are the chief sources of information.

SIERRA LEONE. The Geological Survey of Sierra Leone publish bulletins and annual reports (since 1928). A useful summary of the geology and mineral resources of this territory has been prepared by J. D. Pollett (*Colonial Geol. Min. Resources*, 2, 1951).

SOMALILAND (BRITISH). In 1933 W. A. Macfadyen published an account of the geology of British Somaliland to which reference should be made for general information (Crown Agents, London).

SOMALILAND (FRENCH). Geological information on this territory is restricted. The Carte géologique de la Côte Française des Somalis (Imprimerie Nationale, Paris), 1946, may prove helpful.

SOMALILAND (ITALIAN). G. Dainelli's book *Geologia dell' Africa orientale* (Reale Accademia d'Italia, Rome), 1943, contains a general account of the geology of this country.

SUDAN. The Geological Survey in this territory (Khartoum) publishes bulletins (since 1911). See also G. Andrew, *Geology of the Sudan in Agriculture in the Sudan* (Oxford Univ. Press), 1948, Ch. 6.

TANGANYIKA. The Geological Survey (Dodoma) publishes bulletins (since 1927), various papers and annual reports (since 1928) and pamphlets (since 1939). See particularly *Bull.* 20, 1948.

TUNISIA. The Geological Survey of Tunisia (Service de la carte géologique de Tunisie), Tunis, publishes Annales des Mines et de la Géologie (since 1947). Also the Report of the International Geological Congress (19th session, 1952), should be consulted.

UGANDA. The Geological Survey of Uganda (Entebbe) publishes memoirs (since 1926), bulletins (since 1933), records (since 1950) and annual reports since 1920. See also K. A. Davies and C. B. Bisset, *Bull. Imp. Inst.*, 45, 1947.

UNION OF SOUTH AFRICA. Official publications on the geology of the various countries constituting the Union is the province of the Geological Survey of South Africa (Pretoria) and these range from memoirs (since 1906, formerly Transvaal Geological Survey), special publications on mineral resources and bulletins of the Mines Department, geological series, since 1934. Transactions and Proceedings of the Geological Society of South Africa, Johannesburg (since 1896) contain many important papers on minerals and sedimentary rocks. Reference should also be made to A. L. du Toits' *Geology of South Africa*, London, 1939. The International Geological Congress met at Pretoria in 1929 and several valuable papers were subsequently published (*Compte Rendu*, 1930) to which reference should be made.

AMERICA (CENTRAL AND CARIBBEAN ISLANDS)

BARBADOS. See under General Index to Volumes LI-XC (1895-1934), *Quart. Journ. Geol. Soc.*, London.

COSTA RICA. Two standard works, one by C. Schuchert on *Historical Geology of the Antillean-Caribbean region* (Wiley, New York), 1935, the other by K. Sapper entitled *Mittelamerika* (Handbuch der regionalen Geologie 8) 1937, contain information on sedimentary rocks in this country.

CUBA. Geological publications emanate from the Commission del Mapa Geologico del Ministerio de Agricultura, Havana. See also a paper by R. H. PALMER, *Journ. Geol.*, 53, 1945, p. 1.

DOMINICA. A paper by T. W. Vaughan and others entitled *Un reconocimiento geologico de la Republica Dominicana* was published in 1922 by the Servicio Geologico de la Republica Dominicana.

EL SALVADOR. See under Costa Rica (above) for relevant standard works by C. Schuchert (1935) and K. Sapper (1937).

GUATEMALA. See under Costa Rica (above) for relevant standard works by C. Schuchert (1935) and K. Sapper (1937).

HAITI. Relevant publications by the Geological Survey of the Republic of Haiti (Port-au-Prince) are available; see particularly *Geology of the Republic of Haiti* by W. P. Woodring, J. S. Brown and W. S. Burbank, 1924.

HONDURAS. See under Costa Rica (above) for relevant standard works by C. Schuchert (1935) and K. Sapper (1937).

HONDURAS (BRITISH). See under Costa Rica (above) for relevant standard works by C. Schuchert (1935) and K. Sapper (1937).

JAMAICA. The Geological Survey Department of Jamaica publishes bulletins of which one by V. A. Jans deals with economic geology and mineral resources (1951). See also *Colonial Geology and Mineral Resources*, 1, 1950, for a paper by H. R. Hose on general geology of the island and C. Schuchert (1935, as above).

MEXICO. The official publications of the Geological Survey of Mexico (Instituto de Geologia, Cipres) are bulletins (since 1895) and annals (since 1917). For minerals, bulletins of the Instituto Nacional para la Investigacion de Recursos Minerales, Cipres (since 1945) are relevant. Considerable information on oil and sedimentary rocks is to be found in bulletins of the Mexican Association of Petroleum Geologists, Mexico City (since 1949) and also in publications of the Mexican Geological Society, Mexico City, (since 1905). V. R. Garfias and T. C. Chapin's *Geologia de Mexico* (Editorial Jus, Mexico), 1949, should also be consulted. A textbook by J. M. Muir, *The Geology of the Tampico Region Mexico* (Amer. Assoc. Pet. Geol., Tulsa, Oklahoma, 1936) gives a detailed account of the sedimentary rocks here and includes a full bibliography.

NICARAGUA. See under Costa Rica (above) for relevant standard works by C. Schuchert (1935) and K. Sapper (1937).

PANAMA. See under Costa Rica (above) for relevant standard works by C. Schuchert (1935) and K. Sapper (1937).

PUERTO RICO. A general account of the geology of this island will be found in a monograph by H. A. Meyerhoff (*Univ. Puerto Rico*, series B, No. 1, 1933).

TOBAGO. For the geology and sedimentary rocks of Tobago, a paper by J. C. Maxwell is recommended (*Bull. Geol. Soc. Amer.*, 59, 1948, p. 801).

TRINIDAD. See papers by H. H. Suter in *Colonial Geology and Mineral Resources*, 2, 1951, and 3, 1952. *The Geology of Venezuela and Trinidad* by R. A. Liddle (MacGowan, Fort Worth, Texas) 1928, should be consulted (contains bibliography). A paper by V. C. Illing deals with the geology of the Naparima region (*Quart. Journ. Geol. Soc.*, 84, 1928, p. 1).

VIRGIN ISLANDS. The geology and groundwater resources of St. Croix, Virgin Islands are described in a paper by D. J. Cederstrom (*U.S. Geol. Surv., Water Supply Paper* 1067, 1950).

AMERICA (NORTH) WITH CANADA AND GREENLAND

BERMUDA. There is a valuable paper, including heavy mineral petrographic data by E. S. Larsen, on geology and soils of Bermuda, entitled *Bermuda during the Ice Age*, by R. W. Sayles (*Proc. Amer. Acad. Arts and Sci.*, 66, 1931, p. 382).

CANADA. For general references, the chief sources of geological information are the Geological Survey of Canada (Dept. of Mines and Technical Surveys, Ottawa), in their Memoirs (1910 onwards); Museum Bulletins (1913-1946: the geological series is relevant); subsequent to 1946 comprehensive Bulletins; Papers (1935 onwards) concerned chiefly with field investigations. There is also an Economic Geology Series (1926—date) concerned specifically with mineral resources (No. 1, 3rd. ed., 1947 gives a summary of the geology and mineralogy of Canada). The Department of Mines issues periodic Reports (1904—date) on mineral surveys with much geological data. Contributions from learned Societies are to be noted: Transactions of the Royal Society of Canada (Ottawa, Ontario) and Proceedings of the Geological Association of Canada (1947-48—date), Toronto, Ontario.

Next follow the geological survey publications of individual Canadian provinces, which can be conveniently summarized:

Alberta: Research Council Geological Survey Reports, Edmonton.

Brit. Columbia: Dept. of Mines, Victoria, Bulletins.

Manitoba: Dept. of Mines and Natural Resources, Winnipeg, Geological Reports.

Newfoundland: Geological Survey, Dept. of Public Works, Bulletins and Information Circulars (1934—date).

Nova Scotia: Dept. of Mines, Halifax, Annual Reports.

Ontario: Dept. of Mines, Ontario, Annual Reports and Bulletins.

Quebec: Dept. of Mines, Quebec, Geological Reports (1939—date).

Saskatchewan: Geological Survey (Dept. of Natural Resources, Regina), Bulletins (1948—date); see bull. 9 for bibliography; Petroleum Geology Series Reports (1948—date).

The 12th Session of the International Geological Congress (Toronto, 1913) is chronicled in *Compte Rendu* (1914) and *Guides to Excursions* at the time.

GREENLAND. The Grønlands Geologiske Undersøkelse operates from Mineralogisk Museum, Copenhagen, Denmark and publishes Bulletins (1950—date) and Miscellaneous Papers (1948—date). See also publications by the Kommission for Videnskabalige Undersøkelser i Grønland, Copenhagen. There is a *Geologie von Grönland* by L. Koch (in *Geologie der Erde*, Borntraeger, Berlin, 1935) and another dissertation by C. Teichert in *Geology of North America* (Borntraeger, Berlin, 1939). A paper by M. M. L. Parkinson and W. F. Whittard on the *Geological Work of the Cambridge Expedition to East Greenland* in 1929 (*Quart. Journ. Geol. Soc.*, 87, 1931, p. 650) is relevant to this part of the country (contains useful bibliography).

UNITED STATES. The available literature of the science of sedimentology, especially of this petrography, originating in the United States, is of a magnitude commensurate with the vast natural resources of that country and probably excels, at least in quantity, that of any other country in the world. Sources of information are many and varied, ranging from publications of the U.S. Geological Survey and Bureau of Mines, the National Research Council, through similar official bodies in forty-seven independent states, to geological serials, of which germane to this subject are those of the Geological Society of America; Mineralogical Society of America (*American Mineralogist*); American Association of Petroleum Geologists; *American Journal of Science*; *Economic Geology*; *Journal of Geology* and *Journal of Sedimentary Petrology*. This latter serial was the first periodical to be produced exclusively devoted to the study of sedimentation and sedimentary rocks. The first issue appeared in 1931 and was a direct outcome of the activities of the Society of Economic Palaeontologists and Mineralogists, a branch of the American Association of Petroleum Geologists, organized in 1927. Constant reference to this excellent journal is made throughout this text-book and will inevitably be sought by all students of the subject. For full details of the North American bibliography of geology, especially on the official surveys of the independent states, the reader should consult B. Mason¹.

A pioneer in modern interpretation of sedimentary petrology in the U.S. was undoubtedly M. I. Goldman who published petrographies of the Cathoula Sandstone of Texas (1915), of Upper Cretaceous sediments of Maryland (1916) and later an exposition of Salt Dome Cap Rock (1925); his revised interpretation of the origin of cap rock is given in *U.S.G.S. Prof. Paper 175-D*, 1933. Other prominent American investigators who have made an indelible mark in this field are V. T. Allen, particularly in sedimentary mineralogy (1937, 1948-49, 1956); M. N. Bramlette on heavy mineral studies (1934) and stability of species (1941),

¹ *op. cit.*

and K. Bryan on ventifacts (1929-30). D. Carroll has contributed a valuable series of papers to American literature (see also under Australia p. 47) especially on soil mineralogy, sedimentary-rock minerals, heavy mineral correlation, etc. (1947-53). F. Chayes is prominent for his work on petrographic analysis (1944-45), correlation (1949), thin section analysis (1954) and for his book on petrographic modal analysis (1956), the much desired quantitative approach to the subject. In special category, too, do we acknowledge that classic by F. W. Clarke, *Data of Geochemistry* (1924) of which a new edition is long since due; so much in this bulletin (*U.S.G.S.* 770) is still of lasting value to mineralogists and petrologists. L. Dryden successfully adopted statistical methods of correlation and comparison of heavy mineral suites as long ago as 1933-35 and later, with C. Dryden, determined comparative rates of weathering of some common heavy minerals (1946). In the realm of modern methods of chemical, spectrochemical and modal analyses of silicate rocks (1951), with accent on accuracy of technique (1952), the work of H. W. Fairbairn and colleagues, is outstanding and has direct bearing on such procedures when concerned with arenaceous, argillaceous and siliceous sediments.

E. W. Galliher is associated with intensive studies of glauconite (1935, 1939); J. J. Galloway with physical characteristics of sand grains (1919, 1922). Of recent years critical essays on many aspects of sedimentary petrology, e.g. oil, grain-size, coupled with an over-all statistical application to and interpretation of its problems, from the pen of J. C. Griffiths (1946 1955), have provided stimulating advances in technique to which reference to Chapter XVI in this volume will amply testify. For many years past, the name of R. E. Grim has been associated with fundamental research on composition and properties of clays, in which field he is an unquestioned international leader; reference to the bibliography will pin-point many of his more important contributions to these complex rocks in recent years and his *Clay Mineralogy* (1953) is now a standard text on this subject, one constantly consulted, particularly with regard to structure of clay minerals, X-ray diffraction data, base exchange capacities and optical properties. His publications with R. H. Bray and W. F. Bradley on mica (1937), with F. L. Cuthbert on clay-water properties of certain clay minerals (1945) and with R. A. Rowland on differential thermal analysis of clay minerals (1942) and shales (1944) are all worthy of note. Two significant papers by J. W. Gruner may be mentioned, one on cristobalite in bentonites and fullers earths (1940) and, by contrast, the other on uranium concentration in sediments by migration-accretion (1956).

W. C. Krumbein, throughout a period of many years, has consistently added to the store of knowledge of sediments in respect of their inherent physical characteristics. Originally, his emphasis lay on mechanical analysis (1932-34), size-frequency distribution (1938); graphical and statistical analysis (1939); size, shape and roundness of sedimentary particles (1941); latterly, perhaps, a more pronounced statistical bias to the subject, e.g. latin square experiments, statistical designs for sampling beach sand (1953), application of statistical methods to sedimentary

rocks (1954). With F. J. Pettijohn, his *Manual of Sedimentary Petrography* (1938) has remained a widely read textbook. P. D. Krynine's papers on tourmaline (1946) and field-classification of sedimentary rocks (1948) are, in their respective spheres, likewise directive.

J. H. Martens is perhaps best known for his original contributions on beach sands (1928, 1935, 1939), later on salt deposits (1943); the former work, mainly based on those intriguing Florida shore deposits, set a pattern for much subsequent research into similar beaches elsewhere. B. Mason¹ in his modern *Principles of Geochemistry* (1952) writes a special chapter (6) on sedimentation and sedimentary rocks conceived from a geochemical standpoint. This book firmly spans the wide gap between F. W. Clarke's original *Data*² and contemporary interpretations of the chemistry of the earth. 'Geochemistry,' he says, 'deals with the distribution and migration of the chemical elements within the earth in space and in time'³. This book is an estimable contribution to this fundamental science and, moreover, as an exposition of first principles, is of moment to all students of sedimentology.

To C. Palache, in conjunction with H. Berman, C. Frondel and others, students of mineralogy and petrology throughout the world owe a debt of gratitude for their masterly revision of that classic, *System of Mineralogy* (J. D. and E. S. Dana) now in its 7th edition (I, 1944, II, 1951)⁴, a major American contribution to advancement of this science in recent years and one of which all those involved may be justly proud. It is generally conceded that as a standard work of reference on minerals the Danas' *System* maintains a unique position, unsurpassed by any other treatise extant on this subject. F. J. Pettijohn's work on sediments has included original studies of beach sands (1931) and mineralogy of sedimentary rocks (1932-4, 1936-7). In an important paper he has discussed persistence of heavy minerals and geologic age (1941), while his textbook on *Sedimentary Rocks* (1949) is well known, especially to American students.

K. Rankama and T. G. Sahama published their *Geochemistry* in 1950. B. Mason writes⁵: 'This authoritative and up-to-date book not only treats the general aspects of the subject, but also gives a detailed account of the geochemistry of each element'. Contributions to our knowledge of sediments in various phases, have stemmed from the work of G. Rittenhouse, on heavy minerals (1939), their transportation and deposition (1943), intercept sphericity of sand grains (1943), grain roundness as a geologic tool (1946) and interpretative petrology (1949); with E. M. Thorp he described heavy minerals in sediment-transportation studies (1943). C. S. Ross' latter work has concerned clay minerals (1945), Sauconite (1946); with S. B. Hendricks, studies of the montmorillonite group, their origin and relation to soils and clays (1943-44) and with R. Baldacci, determination of particle size with special reference to kaolins (1951). R. D. Russell's work on Mississippi sands (1936-7), on mineral composition of atmospheric dust at Baton Rouge (1936) and discussion of trends in sedimentology (1949) is also note-

¹ See p. 32.

² *op. cit.*

³ 'Principles', p. 1.

⁴ Vol. III in preparation. ⁵ *Principles of Geochemistry*, 1952, p. 6.

worthy. W. A. Tarr postulated some intriguing ideas on chalk (1925), chert, flint, concretions and cone in cone structure (1930-32) and discussed the origin of some remarkable Lower Permian sand barites in Oklahoma (1933). A. C. Tester is perhaps best known for his dissertations on shape of particles and pebbles (1931-34). F. G. Tickell contributed constructive ideas on the correlative value of heavy minerals (1924); his *Examination of Fragmental Rocks* (1939) is a valued text; with W. N. Hiatt, his paper on effect of angularity of grain on porosity and permeability of unconsolidated sands (1938) should also be noted. P. D. Trask was prominent in earlier years for his contributions on sediments in publications of the Committee on Sedimentation, National Research Council (1930-34); with others, in a symposium on applied sedimentation (1950). W. H. Twenhofel, another indefatigable worker on this subject, is noteworthy for his reports to the Committee on Sedimentation (1926 onwards); but probably his outstanding contribution is the *Treatise on Sedimentation* (1932), a monument of compilation of authoritative data and a basic volume to which every student of the subject must inevitably turn for enunciation of first principles; among his other published researches are papers on environments of origin of black shales (1939), on black sands (1946), on rounding of sand grains (1945), and on environmental significance of conglomerates (1947); with S. A. Tyler his *Methods of Study of Sediments* (1941), is a significant laboratory manual. S. A. Tyler has described bottom samples from the Pacific (1931), coastal sediments from North Carolina and Florida (1934), heavy minerals of the St. Peter sandstone in Wisconsin (1936) and zircon studies in New Jersey highlands (1940).

H. Wadell has added much to our knowledge of shape and roundness of rock particles (1932-33), sedimentation formulas (1934), and volume, shape and roundness of quartz particles (1935). E. E. Wahlstrom, in his *Petrographic Mineralogy* (1955) has written a modern textbook on petrology which contains much of practical and reference value to the student of this subject, including sediments. C. E. Weaver has been concerned with classification of clay minerals (1953) and mixed-layer clays in sedimentary rocks (1956). Physical characteristics of sediments of various grade-sizes have been the theme of much important research by C. K. Wentworth, especially during the period 1919-36. Of particular note are his scale of grade and class terms for clastic sediments (1922); shapes of beach pebbles (1923); studies of coarse sediments (1928); terminology of coarse sediments (1932-4); shapes of glacial cobbles (1936). H. Williams, with F. J. Turner and C. M. Gilbert published a useful *Petrography* (1954). Finally, in the specialized field of mineralogy the names of N. H. and A. N. Winchell will always be associated with *Elements of Optical Mineralogy*, an invaluable reference work, especially to students of sedimentary petrography.

AMERICA (SOUTH) WITH FALKLAND ISLANDS

GENERAL. See *Geologie Südamerikas* by H. Gerth (*Geologie der Erde*, Borntraeger, Berlin), part 1, 1932, part 2, 1935 and part 3, 1941.

ARGENTINA. For a general survey of the geology of this country A.

Windhausen's *Geologia Argentina* (Peuser, Buenos Aires) 1931, should be consulted. Direccion Nacional de Minería, Buenos Aires, is the official survey organization and issues periodic bulletins and other publications, Series B of the former being devoted to geology. The Sociedad Argentina minería y geología (Buenos Aires) issues reviews from time to time as also does the Asociacion geologica Argentina (Buenos Aires).

BOLIVIA. F. Ahlfeld's *Geologia de Bolivia* is a general account of Bolivian geology, published by Instituto del Museo, La Plata, 1946.

BRAZIL. The Divisão de Geologia e Mineralogia, Departamento Nacional da Produção Mineral, Ministerio da Agricultura, Rio de Janeiro, is the official geological authority in this country, responsible for periodical bulletins, monographs etc., while the Divisão do Fomento da Produção Mineral of the Departamento Nacional publishes bulletins and 'avulsos' directly concerned with minerals. A book by A. I. de Olivera and O. H. Leonards (Ministerio da Agricultura, Rio de Janeiro) 1943, is a guide to the regional geology.

CHILE. Information may be sought from the Instituto geografico militar (Santiago) publications (including a geological map 1950) and a general account of the geology of this country is given by J. Brüggen (*Mathematisch-Naturwissenschaftlichen Klasse der Heidelberger Akademie der Wissenschaften*, Heidelberg, 1934).

COLOMBIA. Official publications (bulletins) are those of the geological survey (Servicio Geologico Nacional, Ministerio de Minas y Petroleros, Bogota) since 1952. V. Oppenheim has given an account of geology, including sediments, in a paper on the structure of Colombia (*Trans. Amer. Geophys. Union*, 1952).

ECUADOR. The structure of Ecuador, involving some sedimentary aspects of its geology, is the theme of a paper by V. Oppenheim (*Amer. Journ. Sci.*, 1950). H. J. Tschopp also described the geology of this country in *Vereinigung Schweizerische Petroleum-Geologen und Ingenieure* (1948).

FALKLAND ISLANDS. See A. F. Trendall, *Geology of South Georgia* (Part 1): Scientific Reports of the Falkland Islands Dependencies Survey, No. 7, 1953. References will also be found in Symposium sur les séries de Gondwana, *Inter. Geol. Congress*, Algiers, 1952.

GUIANA (BRITISH). The Geological Survey of British Guiana has published annual reports and bulletins on special subjects since 1933. S. Bracewell contributed an account of the geology and mineral resources of this territory in 1947 (Imperial Institute, London).

GUIANA (DUTCH). An outline of geology and petrology of this colony (Surinam) was published by R. Ijzerman in 1931 (Kernink, Utrecht). Relevant articles occur in *Geologie en Mijnbouw* (1953).

GUIANA (FRENCH). R. Choubert described *Géologie et pétrographie de la Guyane française* in 1949 (office de la Recherche Scientifique, Outre-Mer, Paris).

PERU. The official authority is the Instituto Geologico del Peru, a department of Instituto Nacional de Investigacion Fomento Mineros

Indonesia (Government Printing Office, The Hague), 1949, especially vol. 1A. This covers *inter alia* Andaman and Nicobar Islands, Christmas Island, New Guinea, Phillipine Islands (*q.v.*) and Timor. For Borneo, reference should also be made to *Geology of the Colony of North Borneo* by M. Reinhard and E. Wenk (Geol. Surv. Dept., Kuching, Sarawak), 1951. Java has a Bureau of Mines and Geological Survey stationed at Bandung. W. H. Emmons' *Geology of Petroleum* (McGraw-Hill, London), 1931, contains useful information and references on many of the islands in this vast territory, considered from an oilfield standpoint (Ch. XXI).

IRAQ. An early comprehensive account of 'Syrien, Arabien and Mesopotamien' is contained in *Handbuch der regionalen Geologie V*, 1915, by M. Blanckenhorn. There are also *Geological Notes on Mesopotamia with special Reference to Occurrences of Petroleum* by E. H. Pascoe (*Mem. Geol. Surv. India*, 48, 1924). Much intensive petrographic work carried out in this country during the last three decades or more is buried in the archives of oil companies operating there.

IRAN. An introduction to the geology of this country will be found in a paper by H. G. Busk and H. T. Mayo, *Some Notes on the Geology of Persian Oil Fields* (*Journ. Inst. Pet.*, 5, 1918, p. 3) also in R. K. Richardson's *The Geology and Oil Measures of Southwest Persia* (*Journ. Inst. Pet.*, 10, 1928, p. 256). See also *Contribution to the Stratigraphy and Tectonics of the Iranian Ranges* by H. de Böckh, G. M. Lees and F. D. S. Richardson (*Brit. Assoc.*, 1928). There is a wealth of information on the sedimentary rocks of the Mesopotomian—S. W. Persian geosyncline in a report by H. de Böckh, S. L. James, G. M. Lees and F. D. S. Richardson published by the then Anglo Persian Oil Co. Ltd., (London, 1925—private circulation). R. Furou published a paper entitled *Géologie du plateau Iranien* (*Mem. Mus. national d'histoire naturelle*, Paris, nouvelle serie 7, 1941). Again, a vast amount of data on sedimentary rocks in this region has been accumulated over the years by the chief operating oil companies, much unpublished.

ISRAEL. There is a geological survey in this country, Geological Institute, Jerusalem, responsible for a series of official publications. See also *The Geology and Mineral Resources of Palestine* by S. H. Shaw (*Bull. Imp. Inst.*, 46, 1948, p. 87) and *Oil Prospects of Israel* by M. W. Ball and D. Ball (*Bull. Amer. Assoc. Pet. Geol.*, 37, 1953, p. 1).

JAPAN. Japan has maintained extensive geological activities and publication facilities for many years past. The Geological Survey (Hisamoto-Cho, Kawaski-Shi) has issued reports (1922—date) and bulletins (1950—date). The Geological Society of Japan (formerly of Tokyo) publishes serial journals (1894—date) at the Geological Institute, Faculty of Science, Tokyo University. From this Institute, T. Sakamoto has contributed a Short Report on the Progress of Sedimentology in Japan (since 1949) (*revue de l'Institut Française du Pétrole*, 10, Supplement, Paris 1955, p. 69); this contains an excellent bibliography biased to sedimentary rock studies. Other learned societies concerned with geological serials are the Earthquake Research Institute bulletins (1926—

date) quartered at Tokyo University; Faculty of Science, Hokkaido University, Sapporo, journals (1930-31—date); Faculty of Science, University of Tokyo, journals (section II), (1926—date); College of Science, Kyoto University, memoirs (series B), (1924—date); Geological Institute of Tohoku University, Sendai, serial reports (1921—date).

JORDAN. See paper by A. M. Quennell on *The Geology and Mineral Resources of (Former) Trans-Jordan*, (Colonial Geology and Mineral Resources, London), 1951.

KOREA. A useful sketch of Korean geology is given by T. Kobayashi (*Amer. Journ. Sci.*, 26, 1933, p. 585).

LEBANON. See under Syria.

MALAYA. The Geological Survey (Batu Gajah, Malaya) publishes memoirs (1937—date) and annual reports (1946—date) containing information on sediments. *The Geology of Malaya* by J. B. Scrivenor (Macmillan, London), 1931, should also be consulted.

PAKISTAN. The Geological Survey functions from Quetta and publishes records (1950—date). See also memoirs of the Geological Survey of India (pre 1947) which concern areas in Pakistan, and general references under India (above).

PHILIPPINE ISLANDS. The geology and mineral resources of these islands have been described by W. D. Smith (Bureau of Science, Dept. Agriculture and Natural Resources, Manila), 1924. Another paper by G. W. Corby and others, on the geology and oil possibilities of the Philippines, emanating from the same official source, appeared in 1951. The *Philippine Geologist*, a serial published by the Geological Society of the Philippines (Univ. of the Philippines, Manila) from 1947—date, is relevant.

SYRIA. Probably *Handbuch der regionalen Geologie V*, 1915, by M. Blanckenhorn is the first guide, but since then explanatory texts to the geological map of Syria, Lebanon and northern Palestine (1942) and the *Carte géologique de la Syrie et du Liban* (1945), both published by Délégation Général au Levant France Combattante, Beyrouth, have become available for general geological information.

THAILAND. Consult Geological Reconnaissance of the Mineral Deposits of Thailand (*U.S. Geol. Surv., Bull.* 984, 1951) for information and bibliography.

TURKEY. Official geological publications stem from the Mining and Exploration Institute of Turkey (Maden Tetkik ve Arama Enstitüsü, Ankara) since about 1936. There is also the Geological Society of Turkey (Türkiye Jeoloji Kurumu, Ankara) which publishes serial bulletins (1947-48—date) of regional interest. See also *Handbuch der regionalen Geologie, V*, 1918, *Kleinasien*, by A. Phillipson.

UNION OF SOVIET SOCIALIST REPUBLICS. Since the greater part of the Soviet Union lies geographically in Asia, it is here considered under title of that continent and not under Europe, though it is probably true to say that by far the larger proportion of geological literature emanating from

Russia is conceived and published west of the Urals. Since most geologists are unfamiliar with the language, much that is published in Russian remains a closed book. Of recent years it is gratifying to note that there is a tendency to publish geological papers in French, of which a recent and valuable example to sedimentary petrographers is I. Poustovalov's *Aperçu Sommaire des Principales Études sur la Pétrographie des Roches Sédimentaires en U.R.S.S.*, (revue de l'Institut Française du Pétrole, X, Supplément, Paris 1955, p. 63); this summary covers the years 1949–1954 and contains a detailed bibliography of Russian authors concerned with studies of sediments. The International Geological Congress met at Moscow in 1937 and guide books to the various excursions provide much valuable information on the geology of many regions in the U.S.S.R.; there is also the paper by A. D. Arkhanguelsky on *Structure Géologique et Histoire Géologique de l'U.R.S.S.*, (Rep. 17th Session). W. A. Obrutschew published *Geologie von Sibirien* (Borntraeger, Berlin), 1926, while *The Petroleum Problem of Siberia* is a much later contribution concerning sediments, by D. A. Shanazarov (*Bull. Amer. Assoc. Pet. Geol.*, 32, 1948, p. 153). Most of the geological serials are in Russian and are published by the Academy of Sciences (Akademiya Nauk S.S.S.R., B. Cherkasski 2, Moscow); these include *Geologicheskaya Seriya* (1938—date); *Mineralogo-Geokhimicheskaya Seriya* (1938—date); *Petrograficheskaya Seriya* (1938—date); then there are *Izvestiya (Bulletin) Akademii Nauk S.S.S.R.*, *Seriya Geologicheskaya* (1939—date) and *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva (Mémoires de la société russe de minéralogie, 1866—date)*. To round off this brief survey of the literature, the following works are noteworthy (all in Russian): M. S. Schwertsoff, *Petrography of Sedimentary Rocks* (textbook for mining schools etc.), Moscow, 1934; three by S. G. Sarkissian, *The Minerals of the Sedimentary Rocks* (for the studies of oil-bearing rocks), Moscow, 1954; *The Orientation of Pebbles and methods of their Studies for Palaeogeographical Reconstructions* (Moscow, 1955), and *The Main Features of Palaeogeography of the Devonian Epoch of the Ural and Volga District* (Moscow, 1955). The same author has published quite a number of short papers (in English) bearing on our subject for which reference should be made to *Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS* (1942 onwards).

AUSTRALIA, NEW ZEALAND AND OCEANIA (PACIFIC ISLANDS)

AUSTRALIA. Official sources of geological information are chiefly the various individual state surveys as noted below. There is, however, a Bureau of Mineral Resources, Geology and Geophysics (Canberra) which publishes bulletins (1932—date); summary reports on mineral resources of the country as a whole (1945—date); general reports (1948—date) and quarterly reviews of the Australian mineral industry (1948—date). For an overall picture of *The Geology of the Commonwealth of Australia*, the valuable textbook under that title by T. W. E. David (in three volumes) is recommended (Arnold, London), 1950.

Geological Survey publications of individual Australian states may be conveniently summarized as follows:

New South Wales. Sydney. Bulletins, memoirs, records and mineral resources series.

Queensland. Brisbane. Queensland Government Mining Journal (1900—date) for geological survey data.

South Australia. Adelaide. Bulletins (1912—date).

Tasmania. Hobart. Bulletins: see particularly *The Geology and Mineral Resources of Tasmania* by P. B. Nye and F. Blake (Bull. 44, 1938).

Victoria. Melbourne. The Mining and Geological Journal (1937—date) is the principal official source of geological information.

Western Australia. Perth. The Geological Survey publishes bulletins (1898—date) and annual progress reports (1898—date).

Journals of the Royal Societies of the states, e.g. New South Wales, Western Australia, etc., frequently contain papers dealing with geological matters and petrographic studies. *The Australian Journal of Science* is another serial in which relevant papers appear. As regards individual authors, D. Carroll has been a prolific and original contributor to our subject (sedimentary rocks and soils), as reference to the main Bibliography in this book will soon reveal. Her specialist contributions to this textbook on *Clay Minerals and Soils* (Vol. II, Chs. III and VII respectively) are outstanding (q.v.).

NEW ZEALAND. The Geological Survey operates from Wellington and publishes bulletins (1906—date) and memoirs (1928—date). Much geological information is also contained in transactions and proceedings of the Royal Society of New Zealand (Wellington) and in *New Zealand Journal of Science and Technology* (Dept. Sci. Ind. Research, Wellington).

OCEANIA (PACIFIC ISLANDS). A good general account is by P. Marshall in *Handbuch der regionalen Geologie*, VII (C. Winters Universitätsbuchhandlung, Heidelberg, 1911). The Bernice P. Bishop Museum, Honolulu, has published a number of bulletins on the geology of many of the islands, including Aitu (72); Borabora, Society Islands (169); Cocos (110); Eastern (110); Eua, Tonga (96); Galapagos (110); Lau, Fiji (181); Maiao (105); Mangaia (36); Marquesas (68); Moorea (105); Rarotonga (72); Tahiti (105).¹ For Easter Island, see paper by M. C. Bandy, *Bull. Geol. Soc. Amer.*, 48, 1937, p. 1589; also *Die Geologie der Juan Fernandezinseln* by P. D. Quensel, *Bull. Geol. Inst. Upsala*, 11, 1912, p. 252. The same author has published *The National History of Juan Fernandez and Easter Island* (Almqvist and Wiksell, Upsala, 1952). The geology and petrology of San Felix and San Ambrosio have been described by B. Willis and H. S. Washington (*Bull. Geol. Soc. Amer.*, 35, 1924, p. 365). For Hawaiian Islands, see a paper by H. T. Stearns, *Geology of the Hawaiian Islands* (Div. of Hydrog. Terr. of Hawaii, Honolulu, 1946, Bull. 6). The same author has described the *Samoan Islands* in *Bull. Geol. Soc. Amer.*, 55, 1944, p. 1279.

¹ Numbers in parenthesis refer to bulletins.

EUROPE

GENERAL. For general texts there are *Geologie von Europa* by S. von Bubnoff (in *Geologie der Erde* edited by E. Krenkel), vol. 1, *Eastern Europe and Baltic* (1926), vol. 2 (3 parts), *Western Europe* (published by Borntraeger, Berlin); and *Geologie von Mitteleuropa* by P. Dorn (Schweizerbarts'sche Verlagsbuchhandlung, Stuttgart), 1951.

AUSTRIA. F. X. Schaffer's *Geologie von Österreich* (Franz Deuticke, Vienna), 1951, gives a good general account of the geology of this country. There is an official geological survey (Geologische Bundesanstalt, Vienna) with yearbooks (1850—date), proceedings (1867—date) and discussions (1852—date). The well-known Tschermaks *Mineralogische und Petrographische Mitteilungen*, published at intervals since 1871 (Springer-Verlag, Vienna), is a valuable reference work on mineralogy and petrology. The Geologische Gesellschaft publishes annually *Mitteilungen der Geologische Gesellschaft in Wien* (1908—date) from Theresiengasse 3, Vienna. See also *Geologie und Bauwesen* (Springer-Verlag, Vienna), (1929—date).

BELGIUM. An excellent up-to-date summary, *Travaux publiés en Belgique depuis 1948 sur des questions de Sédimentologie*, by W. van Leckwijck, is contained in *revue de l'Institut Français du Pétrole*, X, Supplément, Paris 1955; this includes a bibliography with over 100 references. The Société Belge de Géologie, de Paléontologie et d'Hydrologie (Brussels) publishes bulletins (1887—date) and memoirs (1903—date). The Société Géologique de Belgique is quartered at Liège and its literature consists of annales, comprising bulletins, memoirs and comptes rendus (1874—date) and separate memoirs (1898—date). See also *Prodrome d'une description géologique de la Belgique* (Liège, 1953) for a general account of the geology of this country. Other sources of information relative to sedimentary rocks are *Annales des mines de Belgique et Institut National de l'industrie charbonnière* (Brussels); *Bulletins de l'Institut Royal des Sciences Naturelles de Belgique* (Brussels), largely palaeontological (1903—date); publications of the 'Association pour l'étude de la Paléontologie et de la Stratigraphie houillères' (Brussels); *Livre Jubilaire V. Van Straelen* (Brussels, 1954); *Mémoires de l'Institut Géologique de l'Université de Louvain* (Louvain); *Natuurwetenschappelyk Tydschrift* (Ghent), for papers on soils. Mention should also be made of the *Revue de Géologie*, first published in 1920 by the Institut de Géologie (Univ. Liège) and valuable as a serial reference to international geological publications.

BULGARIA. The Bulgarian Geological Society (Sofia) has issued reviews since 1927. In 1946 there appeared *Géologie de la Bulgarie* (in Bulgarian) by E. R. Cohen and ors., (Sofia).

CZECHOSLOVAKIA. The official geological survey (Ustřední Ústav Geologický v. Praze, Hladkov 6, Praha) issues a series of publications under title *Sborník* (1921—date); *Vesník* (1925—date); *Knihovna* (1921—date); *Rozpravy* (1929—date); *Geotechnica* (1947—date).

DENMARK. A brief account of the progress of sedimentology in Denmark in the period 1949–1954 is given in *revue de l'Institut Français du Pétrole*,

X, Supplément, Paris, 1955, p. 22, by K. Hansen (in English). The geological survey is the official body (Danmarks Geologiske Undersøgelse, Charlottenlund, Copenhagen), and issues various serials (1890—date) of which series 5 (geological descriptions of special areas, 1930—date) is perhaps most relevant. See also publications of Dansk Geologist Forening, Ostervoldgade 7, Copenhagen.

FINLAND. The geological survey (Geologinen Tutkimuslaitos, Bulevardi 29, Helsinki) publishes bulletins (*la Commission Géologique de Finlande*), (1895—date). *Proceedings of the Finnish Geological Society* (Suomen Geologisen Seuran Julkaisuja, Inst. of Geology, Univ. of Helsinki) should also be consulted for geological information on this country.

FRANCE. There are nearly 400 references in the excellent *Bibliographie des Travaux Sédimentologiques Français Récents* by A. Vatan (*revue de l'Institut Français du Pétrole, Rueil (S. & O.)*, X, Supplément, Paris 1955, p. 29, ranging over the years 1948–1955, and in these the well-known names of L. Berthois, J.-J. Blanc, J. Bourcart, A. Cailleux, M. Dreyfuss, A. Guilcher, L. R. Lafond, C. Razavet, A. Rivière and A. Vatan figure prominently among many other eminent French geologists concerned with field and laboratory studies of sediments. This publication also provides a useful list of local as well as national geological and scientific societies of which France, like ourselves, boasts quite a number. The geological survey (Service de la carte géologique de la France, Paris) issues bulletins (1889—date) and memoirs explanatory of geological maps of France (1893—date). Also relevant are publications of La Société Française de Minéralogie (Masson, Paris); bulletins of the Société Géologique de France (Paris), from which same source emanate *Mémoires de Géologie et de Paléontologie* (1924—date, but previously separated as subjects, dating back to 1833 and 1890 respectively) and *Comptes Rendus Sommaires* (1925—date). L. de Launay's *Géologie de la France* (Librairie Armand Colin, Paris, 1921) is a good overall account of the geology of France.

GERMANY. Here again we turn to the *revue de l'Institut Français du Pétrole*, X, Supplément, Paris 1955, p. 5, for a recent summary of German research on sediments in the contribution by H. Füchtbauer entitled *Kurzbericht Über Sedimentologische Arbeiten in Deutschland Seit 1949*; this includes a detailed bibliography and also a directive to pre-1949 bibliographies on sedimentary rocks (all in German). B. Mason's book¹ gives a very full and up-to-date (1953) account of the various sources of geological information now available. For a short general account, consult *Gründzüge der Geologie von Deutschland* by W. von Seidlitz (Gustav Fischer Verlag, Jena, 1933). The principal official sources of geological information now are Geologische Dienste Berlin; *Geologisches Jahrbuch* (Geologische Landesanstalt der Bundesrepublik Deutschland, Hanover); also State surveys such as Baden (Badische Geologische Landesanstalt, Freiburg); Bavaria (Bayerische Geologische Landesamt, Munich) and Hesse (Hessische Landesamt für Bodenforschung, Wiesbaden). Serial publications include *Geologische Rundschau* (Ferdinand Enke Verlag, Stuttgart), (1910—date); *Heidelberger*

¹ *op. cit.*, p. 83.

Beiträge zur Mineralogie und Petrographie (Springer-Verlag, Heidelberg), (1947—date); *Zeitschrift der Deutschen Geologischen Gesellschaft* (Hanover), (1848—date); and the long established series of *Neues Jahrbuch für Geologie, Mineralogie* etc. (E. Schweizerbart'sche Verlagsbuch-handlung, Stuttgart).¹

GREAT BRITAIN. See under United Kingdom, p. 22.

GREECE. The original official source of information was Service Géologique de Grèce, Athens (1920—1937). This has apparently been superseded by the Institute for Geology and Subsurface Research, Athens, which publishes *The Geology of Greece* (1951—date) and *The Mineral Wealth of Greece* (1951—date).

HOLLAND. De Geologische Stichting operates from Haarlem and publishes memoirs (mededeelingen), (1922—date). For a regional account F. J. Faber's *Geologie van Nederland* (Naeff, The Hague), 1949, should be consulted. Geological serials include *Geologie en Mijnbouw*, published by the Koninklijk Nederlandsch Geologische-Mijnbouwkundig Genootschap, The Hague (1922—date; see June 1951 for a general description of the geology of Holland); also *Verhandelingen, Geologische Serie* (1912—date) and *Mijnbouwkundige Serie* (1912—date).

HUNGARY. The Hungarian Geological Survey, Budapest, issues annual reports and annals of the Hungarian Geological Institute (1882 and 1872—date respectively, also *Geologica Hungarica*, of which Series *Geologica* (1914—date) are relevant. There are also publications of the Hungarian Geological Society (Budapest) entitled *Földtani Közlöny* (1871—date) and the Hungarian Academy of Science (Budapest) issues *Acta Geologica* (1952—date).

IRELAND (EIRF). A recent textbook on the geology of Ireland is by J. K. Charlesworth (Oliver and Boyd, Edinburgh), 1953. The Geological Survey of Ireland is quartered at Dublin and publishes explanatory sheet memoirs to the 1-inch geological maps extant.

ITALY. For recent information on work on sediments in Italy reference should be made to a paper by P. Gallitelli (University of Modena), *Brevi Cenni di Bibliografia Sedimentologica Italiana* (1948—1955), contained in *revue de l'Institut Français du Pétrole*, X, Supplément, Paris, 1955, p. 49. The Servizio Geologico d'Italia (Rome) publishes bulletins (1870—date) and memoirs descriptive of geological maps of this country (1886—date). The Società Geologica Italiana, Città Universitaria, Rome, publishes serial bulletins (1882—date). There is also the *Giornale di Geologica* published by the Museo Geologico di Bologna (1926—date). The Università di Roma, Rome, issues *Periodico di Mineralogia* (1930—date) and the Università di Padova, Padua, the *Memorie degli Istituti di Geologica e Mineralogia* (1912—date).

JUGOSLAVIA. The geological survey (Zavod za geoloska istrazivanja MR Szbije, Belgrade) publishes *Geoloski Vesnik* (1932—date) and formerly

¹ *The German-English Geological Terminology*, by A. Cissarz and W. R. Jones (Murby, London), 1931, is a helpful guide to students of German geological literature.

memoirs (1933–37). Reference should also be made to *Annales géologiques de la Péninsule Balkanique* (Institut Géologique de l'Université de Beograd, Belgrade), 1889—date.

LUXEMBURG. There is a geological survey (Service géologique de Luxembourg, Luxembourg) with serial publications (1937—date).

NORWAY. The official geological publications emanate from Norges Geologiske Undersøkelse at Oslo (1891—date). See also *Norsk Geologisk Tidsskrift* (published by Norsk Geologisk Forening, Geologisk Museum, Oslo), (1905—date).

POLAND. Bulletins of the geological survey (Pantwowy Institut Geologiczny, Warsaw) are available since 1920–22, with a new series 1938—date. A summary account (with references) to the petroliferous deposits will be found in W. H. Emmons' *Geology of Petroleum* (McGraw-Hill, New York), 2nd ed., 1931, p. 630. The Geological Society of Poland, Cracow, publishes annals (irregularly since 1921). Refer also to the archives of mineralogy published annually since 1925 by the Society of Sciences and Letters of Varsovie (Archiwum Mineralogiczne Towarzystwa Naukowego Warszawskiego, Warsaw) and to the quarterly *Acta Geologica Polonica* (Museum Ziemi, Warsaw), published since 1950.

PORTUGAL. The geological survey (Direccas Geral des Minas e Servicos Geologicos, Lisbon) issues *Communicacoes* (1883—date). There is also the Service de Fomento Mineiro at Oporto which publishes *Estudos, Notas e Trabalhos* (1945—date) and *Relatorios* (1941—date). The Geological Society of Portugal (Sociodade Geologica de Portugal, Oporto) publishes bulletins (1941—date).

RUMANIA. The geological survey headquarters at Bucharest (Institutulul Geologic al Romaniei) publish annals, comptes rendus and memoirs. The more intensive work on sediments, especially Tertiary, has been centered on the southern Rumanian oilfield region (see K. Krejci, *Der Bau der Rumanischen Oelgebiete*, *Petroleum Zeit*, 21, 1925, p. 1317).

SPAIN. For a general account of the geology of Spain La Peninsule Iberique by R. Douville in *Handbuch der regionalen Geologie*, 3 (C. Winters' Universitätsbuchhandlung, Heidelberg, 1911) is still a useful guide. From a more strictly and recent sedimentary standpoint, O. Riba's *L'Avancement de la Sédimentologie en Espagne depuis Cinq Ans* (in French in *revue de l'Institut Français du Pétrole*, X Supplément, Paris 1955, p. 23) should be consulted; it contains a summary of researches into sediments, including soils, undertaken by several Spanish geologists (1950–1955) and quite a good bibliography. The geological survey (Instituto Geologico y Minero de España, Madrid) publishes bulletins (1874—date), memoirs (1873—date), notes and communications (1928—date). The Instituto de Investigaciones Geologicas Lucas Mallada, Madrid, since 1945, issues *Estudios Geologicos*, to which reference should also be made. The International Geological Congress met at Madrid, 14th Session, 1926, and *Comptes Rendus* appeared in 1927–28.

SPITZBERGEN. See *Geologie von Spitzbergen, der Bareninsel des König Karl—und Franz-Joseph-Landes* by H. Frebold (in *Geologie der Erde*,

Borntraeger, Berlin, 1935). Refer also to *Quart. Journ. Geol. Soc.*, General Index to Vols. LI-XC (1895-1934), p. 301.

SWEDEN, R. Sanderegren has contributed *Travaux Sédimentologiques Suedois Recents* to *revue de l'Institut Français du Pétrole*, X, Supplément, Paris 1955, p. 52, which spans the years 1949-1953. The several references are annotated, chiefly in English. The textbook is *Sverges Geologi* by N. H. Magnusson, E. Granlund and G. Lundquist (Norstedt, Stockholm), 1949. Official relevant publications of the geological survey (Sveriges Geologiska Undersökning, Stockholm) are Series C (reports and bulletins, 1868—date) and Series Ca (monographs, 1900—date). Of serial publications there is the well known *Bulletin of the Geological Institution of the University of Upsala* (1892—date), containing many papers on sediments and their petrography; also *Arkiv för Mineralogi och Geologi* (Kungliga Svenska Vetenskapsakademien, Stockholm), (1903—date); and *Geologiska Föreningens i Stockholm Förhandlingar* (Stockholm), (1872—date). The international Geological Congress met at Stockholm (11th Session, 1910) and *Comptes Rendus* was published in 1912.

SWITZERLAND. From the University of Geneva, A. Carozzi has contributed a summary of the *Principaux Travaux de Sédimentologie* 1948-1954 to *revue de l'Institut Français du Pétrole*, X, Supplément, Paris 1955, p. 61, which should be consulted for the references to various authors. The official organizations are Schweizerische Geologische Kommission, Basle, concerned chiefly with *Beiträge zur Geologischen Karte der Schweiz*, and the Geotechnische Kommission der Schweizerischen Naturforschenden Gesellschaft, Zurich, which is responsible for *Beiträge zur Geologie der Schweiz*, in particular *Geotechnische Serie* (1899—date) and *Kleinere Mitteilungen* (1931—date). The *Schweizerische Mineralogische und Petrographische Mitteilungen* is published by Schweizerische Mineralogische und Petrographische Gesellschaft, Zurich (1920—date) and is a valuable source of information on these subjects. See also A. Heim's *Geologie der Schweiz* (Tauchnitz Verlag, Leipzig) in two volumes (1919, 1922), a comprehensive textbook.

The debt which industry owes to science is constantly stressed in contemporary speech and writings. There is equally the other side of the story, the progress in academic thought and activity for which industrial demands are directly or indirectly responsible. With geology and particularly sedimentary petrology, the obligation to economics is real and should be properly acclaimed. In his report to the Committee on Sedimentation (U.S.A.) as long ago as 1934, the author wrote: 'I am convinced from long experience that the greatest and most speedy evolution of knowledge of our subject can only be anticipated from recognition of its actual and potential services to the community. Descriptive stratigraphy has its place in academic knowledge, and it is proper that it should always maintain this place, that it should be studied impartially with no material aim other than

to confirm or establish new principles on which geological science rests. Such description, to whatever detail it may go in the matter of component sediments, does, unless carefully watched, tend to become a matter of monotonous repetition; the monotony is immediately broken, however, by discovery of something hitherto unknown by assemblage of facts leading to new trains of thought and activity and when, as a result of broader investigation, the data are capable of influencing some aspect of everyday life. I firmly believe that just as a community comes gradually to accommodate itself to new conditions and values of life, so in outlook must the geologist, in particular the sedimentary petrologist, shift his attitude to the science and hence make his work for it more in accord with the demands of the times'.

That is more than ever true to-day. Each year witnesses an increase in the number of adherents to this branch of geology from all seats of learning throughout the continents of the world. Encouraging as this is, the student should approach his work with a twofold goal in view, that of advancement of geological knowledge and of making that knowledge available for the common good, wherever its practical application may find outlet.

There is just one danger to be guarded against; that, notwithstanding many and varied expositions of first principles, purely analytical phases of the subject as treated in this book may assume prominence out of all proportion to their actual worth; it is useless amassing quantities of facts without seeking to reconcile them with hypotheses capable of explaining their significance, thus contributing to the development of the science; if theory lags behind practice, the result must inevitably be to retard rather than to advance evolution of knowledge, no matter what branch of natural science is involved.

It is therefore necessary at the outset to stress the importance of the more fundamental aspects of sedimentary petrology, in particular the influence that its study has had and will continue to have on progress of pure and industrial geological research. The fact that a large part of this book is concerned with descriptive mineralogy, petrology and laboratory technique should in no way cloud the true perspective of the subject; the determination of the mineral constitution of sediments is but a means to an end; it is the first stage towards unravelling their history and getting to know everything there is to be learnt about them.

CHAPTER II

SAMPLING, PACKAGING, LABELLING, DISPATCH, STORAGE, RECORDS

Sampling (General)—Sampling (Geological)—Sampling (Economic)—Auger Samples—Portable Power-Driven Borehole Samples—Bit-Samples—Bailer or 'Shell' Samples (Cable-Tool System)—Rotary System Core Samples—Reverse Circulation System (Rotary) Samples—Diamond Drill Cores—Packaging—Oilfield Sample-Container—Labelling of Samples—Dispatch—Permanent Storage—Key-Samples—Records: Sample-Indexing—Sampling from Bulk for Laboratory Analysis: Quartering—Sample Splitter—Quantities and Sizes: Sundry Materials and References.

SAMPLING (GENERAL)

SAMPLING is an art in itself no matter what the material concerned. A sample is, by definition¹, the 'small separated part of something illustrating the qualities of the mass etc., it is taken from, specimen, pattern . . .' etc. The art lies in ensuring that the illustration is a faithful representation, not a random caricature, of the original; it implies a certain knowledge of characteristics of diverse materials, natural and synthetic, and, above all, experience in applying the principles involved.

Sampling in its broadest sense may mean anything from arbitrary collection of fossil-, mineral- and rock-specimens in the field to precision procedure where the mathematical element enters into the technique to ensure that a proper ratio is maintained between the part taken and the mass left behind. Clearly procedure must necessarily vary with nature and quantity of material to be sampled: herein lies the secret of success and qualification.

With the rapidly expanding aims of standardization of raw materials in the international field, sampling procedure has become increasingly mandatory. Sampling clauses in British Standard Specifications, for instance, have become quite unequivocal as to

¹ *Concise Oxford Dictionary.*

what should be done to obtain true, representative material, both in quality and quantity, for such analysis or testing as may be appropriate to the subject of the specification. The same thing applies to British Government specifications, *e.g.*, Air Ministry and Ministry of Supply (D.T.D. and C.S. issues). In the United States, the comprehensive and voluminous standards published by the American Society for Testing Materials (ASTM), extending to seven volumes in the 1952 edition alone, lays great and wordy stress on exactly how samples of raw and manufactured materials must be taken, with emphasis on quantity relative to bulk, precise conditions under which such quantity is arrived at, often with information as to what is to be done with the said samples when they have been taken (storage etc.). Much the same rules are laid down for sampling in European and other countries which, with the years, have become more and more 'standard conscious'.

In a memorandum published by British Standards Institution¹, statistical implications are given which underlie certain sampling clauses in specifications; recommendations are also made upon which 'sound sampling clauses can be based'. This again underlines the importance attaching to the subject.

In short, sampling is today a study in itself, one which must be mastered thoroughly in all fields of investigation of natural as well as fabricated materials; to no one is this study more vital than to the sedimentary petrographer who, from the very nature of his raw material, must perforce base both analyses and deductions on such infinitesimal parts of a vast and variable earth-mass at his disposal.

SAMPLING (GEOLOGICAL)

Comprehensive sampling of either consolidated or incoherent sedimentary rocks is at the outset a matter of great importance and one requiring systematic practice and care. Extensive deposits in the field can only be sampled satisfactorily providing there are numerous natural and artificial exposures accessible; this will obviously vary with the nature of the country in which investigations are being carried out.

Surface sampling, as distinct from subsurface sampling, should be effected at chosen intervals along and transverse to the strike of the beds, such intervals depending on the extent of the deposit, persistency of lithological facies, and topographical and structural considerations. Sampling in vertical sections exposed by quarries, cuttings, etc., involves collecting material from horizons determined primarily by change of lithologic facies and of texture of the

¹ Memorandum on sampling clauses in specifications for manufactured articles, PD488 · 1946.

rock. Where vertical sections are absent, samples collected superficially (unless the beds possess a marked regional dip) can only represent a very average composition of the horizon outcropping and will in themselves be little criterion of the nature of the concealed beds; under such conditions 'pitting' may be necessary for the production of samples within 20 ft. or more of the surface, depending on local conditions; failing that, a portable boring apparatus must be employed (see under AUGER-DRILL SAMPLES, p. 58).

Surface sampling involves in each instance the taking of adequate amounts of material from proximate points to make up one sample which will be representative of the particular locality chosen, providing some degree of homogeneity of deposit is in evidence; rapid lateral variation will necessarily narrow down the limits within which this form of sampling may safely be employed.

Samples of incoherent material, such as sand, can most conveniently be collected in the field in numbered canvas bags (convenient size 9 in. \times 6 in. with tapes to tie), each capable of holding about 1,500 g. of material, or the more expensive polythene bags, available in various sizes, are ideal for the purpose. Care should be taken to record the bag number, precise locality, and horizon from which the sample is taken, both in a separate notebook and on a paper slip inserted in the bag. In collecting from a given exposure as, for instance, from a bed of sand 3 ft. in thickness, and in order to obtain as representative a sample as possible from this bed, the bag should be held open against the face and at the bottom of the bed and a geological hammer used to remove material by drawing it from the top of the bed downwards, the dislodged sand thus falling into the bag. Where there are several feet of rock exposed, this method can be repeated from one horizon to another, providing the whole section is accessible.

For subsurface sampling in depth, the geologist has to rely entirely on material taken from borings (oil, water, etc.), and the efficacy of such sampling will depend largely upon the system of drilling employed. Abrasive methods normally yield core-samples and these are the most valuable and easiest to deal with from the geological standpoint. Percussion methods using the 'chisel' (cable-tool system) are specially adapted to oilfield and water-boring requirements and sampling, by means of a bailer or 'shell', can usually be carried out. Samples thus obtained, however, are 'cuttings' or comminuted rock, often unreliable as to precise horizon and actual lithology. The rotary system of drilling, especially if employing mud-flush, unfortunately often precludes all chance of obtaining uncontaminated samples from washings in the 'ditch', notwithstanding frequent assertions to the contrary; much greater

use is now made of core-drilling by this system which has gone far to obviate this disadvantage (p. 62).

Plastic rocks, such as clays, obviously do not lend themselves to the foregoing methods of sampling, the material usually having to be cut out with a knife. It should be borne in mind that much larger samples of clay are required for a proportionate yield of heavy minerals than in the case of sand; also that *the coarser the sand, the larger the sample necessary*, if a reasonable yield of heavy mineral residue is sought.

Consolidated sediments, *e.g.* sandstone, shale, limestone, as is the case with igneous and metamorphic rocks, must be hammered out in the usual way, the material being subsequently crushed if the accessory detrital minerals are required.

Take care always to obtain unweathered samples unless the weathering 'shell' forms part of the investigation in hand.

An intriguing example of intensive geological sampling, largely surface, has been described by P. Allen¹ in the course of his investigation of Wealden petrology. Two horizons in Ashdown Sand, exposed over an area of about 700 square miles in the Weald of Kent, Surrey and Sussex, were studied in mineralogical and statistical detail, based on 107 and 65 (random) subsamples respectively (*i.e.*, representative pieces taken from collected bulk field samples) representing 173 localities (including 272 exposures). He remarks: 'In no case is the assumption made that sampling information necessarily represents geological reality. Sampling data are linked with the unknowable truth, which they estimate, only through probability statements based on objective statistical analysis.'

H. W. Shadle and J. C. Griffiths² carried out investigations into the Pocono Formation outcropping over a large area of Pennsylvania to differentiate oil-bearing from barren Mississippian sediments; this involved a scheme of surface sampling on a big scale and the results are most informative.

SAMPLING (ECONOMIC)

Fundamentally, rock-sampling for any geological purpose, academic or economic, has the same end in view: to procure adequate material for petrographic analysis leading to elucidation of problems in earth-history, stratigraphy, mineral disposition, and so on. In prospecting for minerals, in which may be included, for example, certain types of clay, coal, gravel, limestone, mineral ore deposits, oil and water, evolution of methods of sampling, particularly of the tools involved in the process, has progressed with the times

¹ Wealden Petrology: The Top Ashdown Pebble Bed and the Top Ashdown Sandstone, *Quart. Journ. Geol. Soc.*, **104**, 1948, p. 257.

² An Attempt to Establish Oil Reservoir Favorability Criteria Based on Quantitative Petrographic Analysis. Dept. of Mineralogy, Pennsylvania State University.

at an almost unbelievable rate. To commercial applications of geological science, is owed much modern engineering equipment which has transformed old 'hit and miss' habits of sampling into highly skilled, precision operations. To this extent modern methods of 'economic' sampling are entitled to recognition and account on their individual merits; it is the purpose of this section of the chapter to discuss briefly the more popular hand- and machine-operated sampling gears in use today.

AUGER SAMPLES

The auger is the universally popular hand-boring outfit although in certain instances, where relatively deep holes are required, it may be adapted for mechanical operation. During the course of field-survey, where information is sought in critical places concerning superficial deposits, *e.g.* for foundations, footings, etc., or solid rock beneath subsoil or alluvium, this device for procuring rapidly the desired samples has long been in use. In the early days of Wealden geology, the officers of the Geological Survey used to arm themselves with an instrument akin to a 'cheesetaster' (as it was called), with which subsurface evidence was often quite satisfactorily obtained. From time to time various hand-drilling instruments have been used for a similar purpose, as for example, those described by A. C. Veatch in connexion with hydrological surveys in Louisiana¹. V. C. Illing introduced and developed the use of auger-drilling in Trinidad and the simplicity and efficiency of this instrument—simply a carpenter's auger attached to a suitable length of gas-pipe provided with a T-piece and rod for turning—has made it a most efficient method of obtaining relatively shallow subsurface samples of soft rocks such as clay, sand, silt, marl, etc. Its use is not practicable with hard rocks or with coarse, loosely consolidated materials such as flint-gravel. Holes up to 20 ft. or more are possible by hand-turning alone, depending on the nature of the rocks traversed; the use of a tripod and winch with suitable pulley to aid in hoisting the pipe out of the hole enables far deeper borings to be made successfully.

The auger sets used by the author's survey staff vary in bit diameter according to the nature of the ground to be penetrated and size of samples required. The most favoured bit sizes are 1 in., 1½ in., 1¾ in. and 2 in.². Anything larger than 2 in. is difficult to manipulate by hand at depth. Each auger is adapted at the top end of the shank with screw thread to which the gas barrel (1 in. diameter

¹ Water Resources in N. Louisiana &c., *U.S. Geol. Surv. Prof. Paper*, 46, 1906, p. 93.

² See B.S. 2054 : 1953, Augers and Auger Bits; also B.S. 1978 : 1953, Bit Braces.

standard for all bit sizes) is attached by means of threaded collars. The barrel is in 2 ft. lengths to facilitate the operation of either going deeper or pulling out. The T-piece screws on to the barrel and the tommy-bar ($\frac{1}{2}$ in. steel), inserted in the T, is used for turning. Collars are tightened or loosened, as the case may be, by using 'footprints' or occasionally 'stilsons'. There is a knack in auger boring, and particularly in pulling out without jamming, which quickly comes by experience. When in clay remember that 'short footage then lift' is the best policy in going down, otherwise the bit may stick fast and a difficult and tedious fishing job may follow.

Mention has been made of tripod and winch as accessories to deeper auger boring. Their function is to assist withdrawal of the tool-string. The tripod is constructed of 2 in. scaffold tubing, braced at the apex so as to hold in place a hook to which is attached a pulley over which a wire cable runs from a hand-operated winch. The far end of the cable is secured in the T-piece of the auger-pipe when pulling out. The winch can be affixed to two arms of the tripod, but it is preferable to peg it down into the ground as an independent unit at a workable distance from the rig.

Always keep a good supply of lubricating grease at hand when auger boring; use it generously on bits, collars and T-pieces, on pulley bearings, cable and moving parts of the winch.

With such equipment, holes up to 50 ft. or more, depending on the nature of ground traversed, can be made with comparative ease. Much depends, however, on hand-turning ability in boring deep holes; at least two or three operators are generally necessary to ensure steady progress and to keep the hole plumb.

Samples obtained by the auger are those which are held in place in the convolutions of the bit to which they will readily adhere, especially if the sediment is a little moist; if drilling through dry, loose sand, a slight water-flush will often supply the necessary amount of 'bind'. The sample clinging to the bit should, while still attached, be pared of its outer surface with a knife or suitable scraper, as the superficial material is liable to contamination from the sides of the hole as the bit is withdrawn; it is then recovered in the form of a 'spiral' by running the finger from the cutting point of the bit upwards round the grooves, or alternatively, holding the bottom end of the bit between thumb and finger of the left hand and turning the bit itself in a clockwise direction with the right hand. Exceptionally clean samples, which are invaluable, not only for petrographic purposes, but for checking concealed rocks during the course of field-mapping, can be obtained in this way.

In soil survey procedure, what are commonly known as post-hole augers, 4 in. to 5 in. in diameter, are employed. These are described

and illustrated in Road Research Laboratory publications¹. They may be supplemented by gravel augers, but the latter are not very satisfactory for sampling. Post-hole augers normally go to 4 ft. in depth; thereafter extensions by means of $\frac{3}{4}$ in. gas-piping in 3 ft. lengths are employed. Post-hole augers are supplied with and without self-closing 'flaps' which act as a kind of grab. If used dry, they tend to jam. Where wet deposits are incurred (e.g. below water table), operation is probably more efficient, but even in these conditions jamming is liable to occur and recovery of the tool requires considerable energy. The use of these soil-augers is not recommended in ordinary geological field-work if the smaller diameter corkscrew type will do the job. The R.R.L. soil boring machine, which uses the auger principle on a big scale is briefly described on p. 61.

PORTABLE POWER-DRIVEN BOREHOLE SAMPLES

Midway between hand-operated augers and larger deep-well or borehole, temporary or permanent, cable-tool or rotary rigs, the relatively small portable or transportable power-driven boring plant is extremely valuable for prospecting within comparatively shallow depths. Various designs are available; all must have one factor in common-- appliances for producing proper samples whatever the rocks traversed.

In the space available here it is possible to mention only briefly the several different outfits marketed and used in this country and abroad. Whatever unit is selected, however, it should be capable of yielding ample, uncontaminated subsurface samples, and include tools available to cope with both soft and hard rocks, e.g. overburden resting on solid formation to be drilled up.

One model is the light cable (percussion) drilling rig with aluminium shear legs and sheave, powered by a 3 cwt. petrol-driven hoist. This includes all essential equipment, tools and core samplers. The rig is about 20 ft. high and occupies a 7 ft. square base. Depending on nature of rock traversed, depths up to 100 ft. and more may be successfully entertained and adequate samples secured².

A rather more robust plant is the portable diamond core drill (Edeco, Mark VI) for which is claimed capability to penetrate all formations fast and accurately. The unit is either skid or trailer mounted, employs diamond drill rods of varied diameters ($2\frac{3}{8}$ in. are popular with 3 in. diameter core barrels or drilling bits). Power

¹ D.S.I.R., *Road Research Technical Paper*, No. 15, 1949, p. 5 and plate 3(A). D.S.I.R., *Soil Mechanics for Road Engineers*, London, 1952, p. 137 and fig. 8.3(A).

² Geo. Stow and Co. Ltd., Slough, England.

is by petrol or diesel engines. Depths of drilling with this type of plant are within the 500 ft. to 1,000 ft. range, according to rod-diameter used¹.

The Craelius range of diamond core drills enjoys an international reputation wherever search for economic mineral deposits is prosecuted. Both skid and 'Land-Rover' mounted drills are available. One type (XC-42) with a capacity up to 800 ft., produces cores from $\frac{7}{8}$ in. to 3 in. in diameter. Some of these examined by the author have provided first class material for diagnostic purposes².

Next in the category of portable boring outfits falls the Road Research Laboratory Soil Boring Machine. This is a lorry loaded, diesel-powered unit and can drill holes up to 20 in. diameter, 16 ft. deep, at an average rate of 1 ft./min. in most soils. The cutting tools vary in design according to diameter and nature of deposits penetrated, but the auger principle is broadly maintained³.

Another type of transportable boring apparatus usually restricted to coring concrete roads and runways, but capable of other performances, is the lorry- or tractor-loaded rotary rig with certain special characteristics. An example of this outfit much used by Research Stations and Civil Engineering Contractors for coring concrete, is the Holman core cutter. It 'consists of a Fordson Major Tractor fitted with a Holman core cutter head, which is driven from the rear power take off . . . the tractor can still be used for towing such as pulling water tank or other ancillary equipment. The engine running on T.V.O. is also very economical. It is fitted with four jacks which enable the shot bit to be set up vertical to the road surface enabling a true core to be cut.' The cutting mechanism in this plant is a shot-bit, using chilled steel shot. The concrete is cut wet and usual diameter of core 6 in. Full details are given in a brochure published by the manufacturers⁴.

BIT-SAMPLES

So-called 'bit-samples' or 'drill-cuttings', *i.e.* rock-fragments clinging to the bit of a rotary- or cable-tool and thus recovered, must generally be regarded with suspicion, not only of possible contamination, but often of precise position whence derived; in the absence of other means for taking samples, however, such 'cuttings' must often suffice; they are certainly better than nothing at all. Bit-samples obtained from a rotary-bit are invariably contaminated with mud; those obtained from a cable-tool bit are perhaps more reliable

¹ English Drilling Equipment Co. Ltd., London.

² Craelius Co. Ltd., London; Swedish Diamond Rock Drilling Co., Stockholm.

³ F. G. Taylor and S. Swinney, The Road Research Laboratory's Soil Boring Machine: Recent Improvements in the Design, *Road Note* 1899, 1953.

⁴ Holman Core Cutter, Holman Bros., Camborne, England.

since they are less prone to that particular influence. With samples of this description, a great deal depends upon the type of bit employed, the efficiency of the driller, and the care with which the cuttings are selected, preferably by the geologist.

BAILER OR 'SHELL' SAMPLES (CABLE-TOOL SYSTEM)

These 'cuttings' are frequently all that are available as a record of the rocks penetrated and, in the absence of caving strata or drilling mud, are generally uncontaminated; their reliability as a true index to lithology and horizon may, however, often be a matter of doubt. The cable-tool system, being usually employed for hard rocks, especially limestone, results in the bailer or 'shell' yielding small fragmental samples normally, however, of sufficient size for subsequent production of thin sections.

To a large extent the disadvantages of such cuttings are overcome today by using cable-tool core-barrels which lead to successful recovery of reasonable though often broken cores with practically all types of rock; such core-samples are dealt with in the same way as other cores obtained from rotary drilling systems.

ROTARY SYSTEM CORE SAMPLES

The notable advance made in technique of subsurface stratigraphical identification and correlation, whether dependent on heavy minerals, micro-organisms or study of thin sections, is due largely to the greatly increased facilities for obtaining continuous core samples of the rocks traversed, now offered by modern drilling equipment. In the case of hard, consolidated rocks, cores as recovered should in all cases be comparable with the same materials had they been hammered out *in situ*. Apart from any petrological or palaeontological evidence of the rock succession which such cores may reveal, their use, when properly controlled and interpreted, is of first-class importance in elucidating subsurface structure.

The utility of core samples will depend to a large extent on their diameter, decided by the nature of rock and depth of the boring concerned. In many formations small cores are inadvisable if the larger organisms are sought for evidence, but for obtaining maximum stratigraphical and structural information, anything over 3 in. is in general satisfactory. With 6 in., 12 in., 18 in., or even larger-diameter cores, the geologist should have in all normal circumstances the best material he can expect from otherwise inaccessible rock.

Where soft and incoherent rocks are involved, coring is frequently a matter of difficulty and the recovered samples are apt to be discontinuous, broken and possibly contaminated. Formerly there was

considerable difficulty in obtaining pure samples of such rocks with practically all drilling systems, especially with the rotary where no coring gear was available. Quite an appreciable amount of difficulty encountered in microscopical investigations of such rotary material was traceable to interferent matter from mud-flush, particularly if heavy mineral mud, *e.g.* barite, hematite, was employed for any reason. Modern drilling facilities have considerably decreased such difficulties, though the problem of contamination of soft sand and clay samples, whether in oil or water borings, has frequently still to be faced.

At this point it must be emphasized that, apart from possibilities of contamination with softer rocks, continuous coring of a given borehole, whatever rocks are concerned, while theoretically desirable from a geological standpoint, is not always practicable either on the score of the nature of the rocks penetrated (*e.g.* cavernous limestone, loose detritus) or of expense.

In oilfield practice, unless continuous coring is specified, core-samples are generally taken at regular intervals where little or nothing is known of the subsurface rocks; such intervals may be every 30 ft., 20 ft., 10 ft., or less in exceptional circumstances; where more is known of the rocks being drilled, the intervals may be much greater until critical horizons are reached, such as oil-sands, cap-rocks, etc., when close coring becomes a matter of necessity.

That the use of the core-barrel does not eliminate the contamination factor is due to the fact that drilling mud, if used with rotary system, is liable to 'pack in' with the rock, especially if the latter is soft or when drilling pressure is high. Many core-samples examined by the author have obviously suffered contamination in this way, in some cases the heavy mineral assemblage varying from different parts of the same core. A. C. Rubel¹ has discussed some pertinent aspects of this question of contamination and has shown how in some cases the drilling mud may not only coat the outside of the true rock-core, which frequently happens, but may be forced to penetrate a loose sand, for example, giving rise on compaction to a core of alternate sand and mud, instead of a core of definite sand, with resulting inaccuracy in 'logging' the well, to say nothing of the ultimate petrographic examination. Another case in the author's experience is where the drilling mud itself gets cored, *e.g.* when drilling through fine mobile sand which, masked by the flush, results in the drillers' erroneous record of 'mud', 'shale', 'gumbo', etc.

To guard against misleading appearances and possibilities of this nature, the following precautions should always be taken before

¹ Determination of Core-Samples in Core Drilling, 9th Ann. Rep. Calif. State Mining Bur., 9, 1924, No. 11, p. 5.

submitting cores to treatment for petrographic or other analysis: (a) with soft rocks always scrape off the outer margin of the core; with a 3 in. core, for example, this implies discarding at least $\frac{1}{4}$ in. to $\frac{1}{2}$ in. of outside material; (b) take the interior of the sample for investigation wherever possible; (c) at frequent vertical intervals, as represented by the cores, split a sample longitudinally to ascertain whether any extraneous material (drilling mud) has penetrated the rock; if this has happened it will usually be indicated by the inter-digitation of the mud and the rock, the mud-laminae being continuous with the mud forming the outside coating to the core; (d) if a mud-flush is used in which the mud is obtained from the same supply throughout the drilling of the well, take a sample of the material (silt or clay) employed from time to time and examine carefully as a check on possible impurities. Often the mud employed is furnished by the finer shale- or clay-cuttings obtained during the early drilling of the well so that, unless care is taken, critical constituents of a higher horizon may quite easily find their way into deeper cores and thus be misinterpreted in subsequent examination. It is apparent, however, that the possibility of contamination is greater the softer the rock; on the other hand, with hard rocks other drilling systems may be resorted to and the contamination factor expected to prove far less serious.

REVERSE CIRCULATION SYSTEM (ROTARY) SAMPLES

This is a novel departure from traditional straight mud-flush rotary drilling and, although increasingly used abroad, has only within recent years found favour in the United Kingdom. Briefly, the system consists in drilling with a slowly rotating scraper attached to a drill pipe up which rock-cuttings are sucked by means of a gravel suction pump. Cuttings are delivered in this way to a water-filled pit, where they settle out; from this source relatively clean water flows back into the hole in annular space between drill-pipe and borehole wall. The system is particularly adapted to sand and porous formations and, given the essential supply of drilling water, any collapse of rock-wall is prevented. As far as sampling is concerned, it is claimed for this system 'that the debris removed at the point of drilling is brought to the surface very quickly and without any contamination from other strata; hence samples are extremely accurate'. Full details are given in the reference cited below¹.

DIAMOND DRILL CORES

Where a diamond drill is used, the core-samples are probably less contaminated than those obtained by any other means; in fact,

¹ *Water and Water Engineering*, 60, 1956, p. 252.

except with very loose sediment, this system of drilling provides the geologist with some of the very best material for ultimate microscopical examination. 'The value of the solid core secured by the diamond drill cannot be over-estimated. These cores show in exact sequence the various rock-layers pierced and record accurately the depth, thickness and character of each one, together with its dip and strike. As compared with ordinary drilling methods which merely furnish cuttings brought up by the return water, the diamond drill core represents definite, complete knowledge, the other, guess-work.'¹ Quite apart from the investigation of micro-organic or heavy mineral constituents extracted from such cores by crushing, this form of well-sample lends itself more readily than any other to analysis by means of thin sections.

Core-sample 'splitters' and extractors are supplied as part of the standard coring equipment for all drilling systems.

PACKAGING

It is one thing to have the means to collect satisfactory surface or subsurface rock-samples, but quite another to ensure their safety in transit if and when conveyed from one place to another. Many people have not the remotest idea of how materials inadequately packed suffer in transit; they are frequently the persons who are quite incapable of 'doing up' a parcel properly for posting, let alone securing bulk or weighty packages of samples, etc., for road or rail consignment. Many years' experience of badly-packed samples arriving in the author's laboratories (solids, often of liquids, too) and the trouble caused thereby, are sufficient justification for drawing attention briefly to this aspect of sampling.

Packaging can, of course, mean storage (*q.v.*) in containers best suited to the materials involved and the question of their independent transport may not apply. But where transport does apply, then care must be taken to see that (*a*) breakage or leakage cannot occur; (*b*) nothing rattles; (*c*) the container(s) is adequate for the material to be dispatched; (*d*) the package is securely fastened, be it paper, cardboard, wooden or metal box (or drum) or any other form of container.

For rock-samples, rectangular cardboard boxes with close-fitting lids, *e.g.* sizes 3 in. × 3 in. × 3 in., or 4 in. × 4 in. × 3 in., or 6 in. × 6 in. × 3 in., are most serviceable. Paper sacks (3- and 5-ply cement type) are useful for bulk samples, *e.g.* asphalt, tarmacadam, mineral aggregates, etc. (only half fill each sack and if by any chance there is likelihood of exposure to moisture or rain, enclose each sack and contents in an outer hessian sack). Wooden boxes and

¹ Diamond Drilling for Oil, Sullivan Machinery, Chicago, 1923, p. 9.

crates, if heavy (*i.e.* over 20 lb.) should be externally metal- or wire-strapped. Similarly metal drums, especially those containing fluids, should be 'crated' with upright wooden slats secured top and bottom, to prevent damage by impact of other goods in transit. Glass containers should always be carefully wrapped in paper, then well and truly immersed in excess sawdust and finally properly packed in wooden boxes. Much of all this is really common sense, but it is of sufficient importance to justify foundation of the Institute of Packaging in this country (1947) which provides a forum for people from all sorts of industries concerned with packaging problems. 'Packaging has "untidy boundaries"'¹, a remark applying equally to the technique as to innumerable different packages as such.

All the materials with which this book is concerned deserve to be tidily packed: that is a *sine qua non* of experienced sampling. Reference to B.S. 1133 and its several sections (especially 1-3, 7, 8, 9, 10, applicable to our subject), comprehensive in its treatment of this most important matter, is strongly recommended.

OILFIELD SAMPLE-CONTAINER

For hard or repeated use, ordinary canvas bags or unprotected tins are of little use as sample-containers and in oilfield practice it is customary to employ a strong pattern wooden container for transporting samples from drilling wells to the laboratory, also to prevent as far as possible any mixing of materials either on the derrick-floor or subsequently during conveyance. This type of container is so consistently successful that it may with advantage be used in other circumstances where systematic sampling is contemplated.

The pattern recommended by the author consists of a flat, shallow wooden box, with lid, constructed externally of $\frac{1}{2}$ in. or $\frac{3}{4}$ in. white wood (teak for the tropics) and of such dimensions that it may be subdivided inside by $\frac{3}{8}$ in. partitions into twelve cells, each cell being capable of accommodating either a rectangular tin 3 in. \times 3 in. \times 4 in. or a round cigarette tin (50 size); both forms of tin should have lids. The container is fitted with substantial hinges and fasteners and a handle, usually of leather, is attached to the front in a similar position to the handle of an attaché case.

For core-samples special open rectangular wooden trays, longitudinally partitioned, are generally employed. These depend for dimensions on the diameter of the cores taken. In the case of 3 in. cores, for example, the convenient tray is one which accommodates in six divisions 36 ft. of core, *i.e.* 6 ft. per division. More core per tray, especially if the diameter is larger, results in very heavy,

¹ Institute of Packaging, Organization and Objectives. London, 1954, p. 3.

unwieldy containers, though where labour is not difficult this may be no drawback. Such core-trays are used both on the wells and for permanent storage.

LABELLING OF SAMPLES

A word of warning is necessary in cases where no core-trays are employed. Ordinary drilling practice, especially with borings for water in this country and elsewhere, is to mark at convenient, though often irregular, intervals the recovered cores, usually with an indecipherable dab of black paint, either numerals or hieroglyphics being employed, to represent depth in feet. The cores are then laid out in more or less parallel lengths alongside the rig, exposed not only to the vicissitudes of weather, but to the deprivations of all and sundry who suddenly want some lumps of rock for weighting down tarpaulins, corrugated iron, or for other purpose on site, or of those whose nearby gardens or allotments may secure some adornment by perquisites of an unusual character.

Unless very strict instructions are given, the last thing the driller usually worries about is the cores; the geologist, if he is not continuously on the job, may soon find that half the value of careful coring during the progress of the work is destroyed by inability to mark correctly, place properly, and guard cores once taken. The author writes from bitter experience of this kind of thing and also with a wholesome distrust of the memory of the drilling crew, who may afterwards attempt to make good the damage by placing the cores correctly [?] in the supposed order of succession.

In all cases where close or continuous coring is decided upon, it is the geologist's duty to advise his principals very definitely regarding the layout of these core samples; in cases where he has a reasonable knowledge of the rocks to be penetrated, it is often possible to instruct the drillers at exactly what intervals of depth to mark cores; alternatively, to mark every lithologic change, whichever is the more appropriate. Furthermore, the marks (numerals) should be made distinctly and with a waterproof black paint (preferably bituminous) specially supplied for the purpose. It should also be made incumbent on the driller to record in his log book the corresponding series of depths at which the samples are marked, quite apart from his usual fanciful description of the rocks penetrated.

When dealing with a large number of samples other than cores, the possibility of confusion has equally to be guarded against. Much trouble of this kind can be avoided by careful and systematic labelling. All samples, whether consolidated rock-specimens or loose material in sample-boxes, bags or other containers, should be

clearly numbered as soon as they are collected, serial numbers in conjunction with an index-letter denoting a given area or locality being preferable; thus differentiation from previously collected material is automatically made. In oilfield practice the field or lease (often signified by a letter of the alphabet or suitable field-sign), the well number and depth, are desirable, *e.g.* 'B.B. 27—1875'; *i.e.* 'B.B.' lease or field, well no. 27, depth 1,875 ft.; the next sample might bear the label 'B.B. 27—1890' and so on. When a given series of samples from the same well is in process of investigation in the laboratory, the depth numbers obviously suffice for reference.

DISPATCH

Destination of rock-samples or any other materials intended for investigation, is in most cases the laboratory and not only the means, but often a desirable limiting time factor, is concerned in their sending. Where direct road transport from site to laboratory is available, this is generally the most efficient and quickest method of getting the samples safely from *A* to *B*. Long-distance freight aeroplanes ensure rapid, although expensive, transport of goods from one country to another, subject always to weight restrictions. In this connexion, several small consignments are often better than one bulky one. With postal dispatch, weight is again a restrictive factor; solids offer no particular difficulty, but caution must be exercised when sending fluids by this means and current Post Office regulations consulted. Rail transport overcomes most dispatch problems, but consigning via 'Goods' often spells undue delay in delivery. Sea-borne samples, unless conveyed on certain regular, fast trans-ocean routes, are liable to lengthy delays, but on the other hand this form of dispatch is safe and still relatively inexpensive in spite of dock, agents' charges, etc.

One factor to be reckoned with in dispatch of samples from overseas is the internationally-enforced customs and excise declarations. It is relevant to remark that, in the author's experience in sending to or receiving petrological materials from overseas, a precise statement of contents on labels *e.g.* 'Rock-Samples' followed by the words 'NO VALUE', *if of course strictly valid*, will often ensure clearance without any official opening of the packages concerned, hence avoiding delay or maybe, what is probably far worse, upsetting tidily packed and often fragile contents such as, for instance, microscope slides.

PERMANENT STORAGE

Methods of storing samples vary largely according to taste, custom, facilities, climatic conditions and the nature of the materials. With

loose sediments or 'cuttings', glass bottles with wide necks and corks, or, better, flat-topped screw-on stoppers (fruit-preserving type) may be employed where visible quantities of material are required. For small quantities, storage is most conveniently effected either by cardboard containers (square with lids or cylindrical with screw tops), strong canvas-lined envelopes, or glass specimen-tubes; the author favours the latter receptacles, especially those with screw metal tops, size 3 in. \times $\frac{3}{4}$ in., 4 in. \times 1 in., 5 in. \times 1 in. or 6 in. \times 1 in.; where cheapness is a desideratum, 4 in. \times 1 in. tubes with flat corks are quite good. Cardboard or canvas containers are apt to be destroyed by insects or mice, especially in hot countries, or they may suffer quickly from damp. Glass has the disadvantage of being liable to breakage; tins resist attacks of insects and to some extent damp, but they quickly rust if not kept in dry surroundings.

Always put an identification label inside the sample-container as well as on the outside.

With core-trays, it is usual to paint or otherwise mark on both ends of the container the field-sign, well number, and limiting depths represented by the cores inside; the boxes are then stored side by side on suitable shelves in such a way that the 'end-labels' can be rapidly read and any given series of cores referred to easily. The cores from one well or boring are always kept together. In the case of larger-diameter cores, this method of storage may prove impracticable; it then becomes a question as to whether the whole core suite shall be kept or, once the necessary evidence is obtained, only representative pieces from critical horizons; in the latter event, the material is usually dumped in an appropriate place or, as may well occur on isolated sites, if the rock is suitable, utilized for local pathway or road construction. Whatever happens, the responsibility should finally rest with the geologist.

KEY-SAMPLES

The advantage of setting aside small portions of important samples for future reference and comparison with material subsequently obtained is sufficiently obvious to require no further emphasis. Such 'key-samples' may be representative of particular stratigraphical subdivisions, zones, horizons, oil-sands, water-sands, prolific foraminiferal clays, etc., and are independent of any microscope slides of mineral residues or organisms ultimately prepared.

Of a similar significance are the specific outcrop specimens collected for purposes of comparison (on analysis) with equivalent rocks likely to be met with in well-samples; see p. 108.

FIELD	X. Y. Z. Co.		SAMPLE NO.	DEPTH ¹
WELL NO.				2190 ft.-2195 ft.
FORMATION	HORIZON		CASE NO.	
SAMPLE ²	BY WHOM TAKEN	DATE	DRAWER NO.	
DRILLER'S LOG ³	COLOUR (W or D) ⁴			
MEGASCOPIC DATA	REMARKS ⁵			
VISIBLE ORGANISMS				
TEXTURE	GRADE	SHAPE	ACCESSORY MINERALS	
MICRO. ANAL. ⁶	THIN SECTION NO.		PER CENT. TOTAL SAMPLE	
			AVERAGE GRADE	
			AVERAGE SHAPE	
			SPECIAL FEATURES ⁷	
(SEE OVER FOR DETAILS) ⁸				

FIG. 1. Specimen Well-Sample Card as designed and used by the author. Actual size 8 x 5 in.

NOTES.—1—Depth-range is inserted boldly in top right-hand corner to facilitate reference when in file. 2—State here whether core, cuttings, etc. 3—Description as entered in driller's log. 4—W = wet, D = dry. 5—Insert here any special observations, e.g. oil, asphalt, etc. 6—Microscopic analysis. 7—Note here any peculiar index-minerals or characteristics of the suite. 8—Reverse side of card used for list of minerals or special data.

RECORDS: SAMPLE-INDEXING

The storage space necessary for accommodation of many rock-samples is liable to grow considerably in excess of laboratory facilities for this purpose; hence some system of indexing or filing information concerning samples soon becomes essential and, in point of fact, is much favoured in laboratories concerned with work of this kind. The samples can be stored outside in a suitable storehouse, shed or similar place, while the card-index is a requisite part of the laboratory equipment. Generally a card is devoted to each sample (in the case of oil-well samples) and contains information regarding field or lease, position, name and/or number of well, depth, geological horizons proved and other relevant data. In some cases a separate card-index is made for recording petrographical and/or palaeontological data obtained from certain samples, for the purpose of rapid reference when carrying out microscopical examination of new material and to save time in searching a number of different and possibly irrelevant slides; or such information may be logged on the one card.

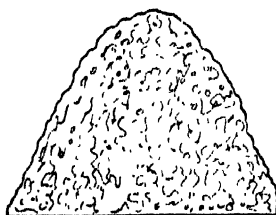
Index-cards and files vary according to requirements; a useful size is 8 in. \times 5 in., which provides enough room (both sides) for all possible information. A suitable standard type for well-samples is reproduced in Fig. 1.

To obtain the fullest use from a card-index system of this character, it should be used in conjunction with graphic well-logs of each well drilled. Incidentally, special samples, water analyses, oil and gas horizons, etc., can be logged on different coloured cards placed in proper sequence with the sample-cards.

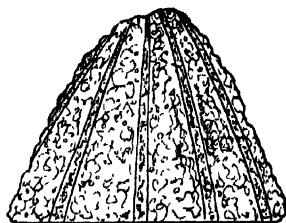
SAMPLING FROM BULK FOR LABORATORY ANALYSIS:
QUARTERING

It is frequently necessary to reduce bulk rock, either lump, crushed, or naturally incoherent, such as gravel, sand, etc., to workable size for laboratory investigation, whether this involves chemical, microscopical or physical tests. In such an event the ultimate sample must be truly representative of the bulk in order that results may reflect inherent properties of the mass as faithfully as possible. To achieve such a sample the utmost care and systematic procedure are important.

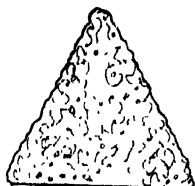
It should be remembered that everything depends on the efficacy of initial sampling. If errors creep into this, analytical results may be entirely vitiated. Further, in certain circumstances it may not be practicable to re-sample the bulk for repeat tests if results are suspect; whereas if the sample is correctly obtained in the first place,



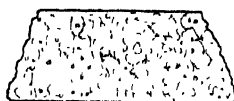
Original Heap.



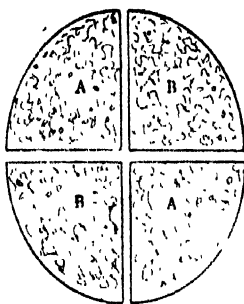
Furrowed Heap.



Cone.



Flattened Cone.



Carving.



Mixed Quarters.
A, A.

FIG. 2. Sampling from Bulk—Quartering.

repeat tests can be made with the assurance that whatever error may have occurred, it is not due to sampling.

Actually scientific sampling of large bulk material is quite a complicated business demanding considerable skill. Some idea of what is involved in extreme cases, both in theory and practice, is obtainable from the specifications for sampling coal¹, to which the reader is accordingly referred. For all practical purposes with ordinary rocks, procedure can be simplified to reduction of bulk by quartering and is determined by the nature of the rock to be sampled, size of the available bulk from which the sample is to be prepared and variation (if any) in size of components. Details of the procedure to be adopted in sampling such materials as sands, aggregates, fillers, solid rock, lump slag, etc., together with information regarding sizes of samples to be taken, will be found in British Standard Specification 812 : 1960, Section 1².

In the case of material of mixed grade such as 'all-in ballast', the following procedure will be found effective. Assume a heap of 5 cubic yards (approximately 5½ tons). Select a series of places at approximately regular intervals round the heap, say every 3 ft. With a shovel remove the outer material from the top downwards to form distinct furrows; such material should be rejected. Then attack each furrow in succession from the bottom, working upwards to get a representative shovelful. Three shovelfuls should be taken from each furrow and the shovelfuls mixed together on a clean, flat surface (Fig. 2).

The next stage is 'coning'. Heap the material obtained into a cone by shovelling small quantities at a time one on top of the other, taking care to keep the cone as true to shape as possible. If desired this coning can be repeated by systematically breaking down the first cone (working from the base) and forming another alongside. Once the final cone is made, flatten by pressing the shovel on to the apex, thus reducing the mass to a flattened pile of circular cross-section and uniform thickness. Next carve the mass through with the shovel with two right-angle cuts so as to divide it into four quarters, separating the material slightly with a lateral movement as the cuts are made. Remove two opposite quarters and reject them. Re-mix the remaining quarters completely in the form of a cone, flatten, re-quarter as before and reject opposite quarters. Repeat the process until a sample of desired size is achieved. In the case of 'all-in ballast' taken as example, it is assumed that sizes range from 2½ in. pebbles down to coarse sand, in which case, from 5 cubic yards an ultimate sample of approximately 2 cwt. would be adequate to submit to the laboratory where, according to the particular tests

¹ *British Standard Specifications* 1016, 1017, 1942.

² *Sampling and Testing Mineral Aggregates Sands and Fillers.*

to be made, it would be re-sampled by crushing, quartering, grading, etc.

It should be realized that in taking samples of material containing a large assortment of sizes, such as above, it is always difficult to maintain and preserve accurately the initial ratio between coarse and fine detritus in the final sample. Great care is necessary to avoid overloading shovelfuls with coarse material which naturally tends to fall from the top of the heap when dislodged. Aggregates of this description should, if possible, never be sampled if exposed to wet weather or if they have lain long in the open, owing to the tendency for finer sand either to be washed down or else to gravitate to the bottom, there to concentrate.

Where grading is more uniform, even of coarse material such as crushed granite or flint or naturally graded, uniform gravel or grit, the above difficulties are less likely to arise and procedure will be as described.

Where crushed rock, powder, sand, or fine, uniform filler is concerned, much the same process is involved. If the initial bulk is small it should be well turned over before commencing to sample. Shovelfuls should be taken at regular intervals, coning and quartering to suit. If the bulk is large, a similar procedure of attacking it at regular intervals around the periphery as described above will be necessary; alternatively, with rock powder, fillers, etc., the material may be sampled with a scoop (about 1 lb. capacity) from various points on the heap, each scoopful being emptied into a cask or suitable container, after which coning and quartering proceed in the usual way. With such material, it is also possible to use a sampling tube, which can be made out of suitable brass tubing in which is cut a longitudinal slit; the bottom end of the tube is tapered and the top end is fitted with a strong handle similar to that on a motor car tyre pump. The tube is inserted at regularly spaced intervals and made to penetrate as deep as it will go. Each withdrawal carries representative material from depth of the mass and this is emptied into a container until the requisite quantity of the substance is obtained for quartering. The tube method is particularly useful for fillers stored in sacks or barrels.

Finely divided material, if of uniform grade, should always be sampled in as dry a state as possible.

SAMPLE SPLITTER

Alternative or even subsequent to quartering with many materials, is the use of a sample splitter or 'riffler', apparatus for separating incoherent material (it must be dry) into truly representative samples. The normal type is a galvanized steel box (mounted on legs) divided

into twelve parallel chutes, each inclined at an angle of 60° , alternately six to one side, six to the other. Materials are decanted from the original container, poured as a stream through the riffler and collected in wooden containers on either side. The process is repeated at will until the appropriate sized sample is obtained. The usual type employed with aggregates follows the design of the Road Research Laboratory¹.

QUANTITIES AND SIZES:

SUNDRY MATERIALS AND REFERENCES

Hitherto no specific mention has been made of quantities and/or sizes of samples of the several raw materials which may be required by analytical and testing laboratories concerned with them. The reason is, of course, that such requirements depend entirely on the nature of these materials and scope of the particular investigations in which they are concerned. However, as a guide to current practice in this country, the following summarized selection of raw materials, products and references will, it is hoped, prove indicative.

One overriding principle in estimating quantities and/or sizes of samples of natural minerals and rocks, or synthetic products fabricated from them, to meet normal laboratory demands, is always to err on the generous side wherever possible. Inadequate samples make the job of analysis or testing difficult, often impracticable in terms of precision in procedure and accuracy of results. Also, as already pointed out, insufficient sample does not permit of repeat tests if results are suspect.

In a majority of cases cited below, the references give both sampling procedure and, if not directly, by inference, because of the analyses or tests relevant to the subject concerned, actual quantities or sizes of materials required. In parenthesis (under references,*) will be found minimum quantities of certain materials as are customarily stipulated in the author's laboratories.

Although British Standards are quoted throughout these references, the reader is strongly recommended to consult the much more detailed A.S.T.M. Standards (1952), in particular Parts 3 and 5, which cover a number of natural raw materials and synthetic products listed on following pages.

¹ D.S.I.R., Soils, Concrete and Bituminous Materials, London, 1946, pp. 177, 215. Concrete Roads, Design and Construction, London, 1955, p. 21 and Plate 2.2(A).

MATERIALS	TYPE OR PURPOSE	REFERENCES
Aggregates	Clinker	B.S.1165 : 1957 (28 lb. min.)*
—	Concrete (natural sources)	B.S.882, 1201 : 1954
—	Building sands (natural)	B.S.1198, 1200 : 1955
—	Mineral	B.S.812 : 1960
—	Single-sized (roads)	B.S.1984 : 1953 B.S.882, 1201 : 1954 (quantity according to size : min. 14 lb.)*
Asphalt	Fine cold (roads etc.)	B.S.1690 : 1950 (12 in. sq. min. or 14 lb.)*
—	Hot rolled (roads)	B.S.594 : 1958 (spec.)
—	Native (lake asphalt, gilsonite, etc.)	B.S.598 : 1958 (sampling) (10 lb. min.)*
—	Natural rock	B.S.348 : 1948 (7 lb. min.)*
—	Tiles (paving)	B.S.1325 : 1946 (3 tiles min.)*
—	Tiles (paving, natural rock)	B.S.1324 : 1946 (1954) (3 tiles min.)*
Asphalt Mastic	Damp-proof, tanking	B.S.1097 : 1958 (12 in. sq. min. or 14 lb.)*
—	Damp-proof, tanking (natural rock)	B.S.1418 : 1958 (12 in. sq. min. or 14 lb.)*
—	Flooring	B.S. 1076 : 1956 (12 in. sq. min. or 14 lb.)*
—	Flooring (coloured)	B.S.1451 : 1956 (12 in. sq. min. or 14 lb.)*
—	Flooring (natural rock)	B.S.1410 : 1959 (12 in. sq. min. or 14 lb.)*
—	Roads, footways	B.S.1447 : 1948 (12 in. sq. min. or 14 lb.)*
—	Roads, footways (natural rock)	B.S.1446 : 1948 (12 in. sq. min. or 14 lb.)*
—	Roofing (limestone aggregate)	B.S.988 : 1957 (12 in. sq. min. or 14 lb.)*
—	Roofing (natural rock)	B.S.1162 : 1957 (12 in. sq. min. or 14 lb.)*
Benzoles	Solvent	B.S.135 : 1953 (1 gal. min.)*

MATERIALS	TYPE OR PURPOSE	REFERENCES
Bitumen — — — —	Native Base-filling compounds (electrical) Emulsion, road Macadam Macadam (gravel aggregate)	(10 lb. min.)* B.S.1858 : 1957 (1 gal. min.)* B.S.434 : 1952 (1 gal. min.)* B.S.1621 : 1954 (spec.) B.S.598 : 1958 (sampling) B.S.2040 : 1953 (spec.) B.S.598 : 1958 (sampling)
Bituminous Mixtures	Roads etc.	B.S.598 : 1958 (sampling)
Bricks —	Clay, building Clay, engineering	B.S.1257 : 1945 B.S.1301 : 1946
Carbon disulphide — tetrachloride	Solvent Solvent	B.S.662 : 1950 ($\frac{1}{4}$ W.Qt.)* B.S.575 : 1957 ($\frac{1}{4}$ W.Qt.)*
Cement — — —	High Alumina Portland—blast furnace Portland—low heat Portland—ordinary and rapid hardening	B.S.915 : 1947 (14 lb. min.)* B.S.146 : 1958 (14 lb. min.)* B.S.1370 : 1958 (14 lb. min.)* B.S.12 : 1958 (14 lb. min.)*
Coal — — Coal and Coke — —	Screen Analysis Size Analysis Size—Weight ratio Sampling and analysis Sampling Testing and analysis, including sampling	B.S.1293 : 1946 B.S.2074 : 1954 (sampling) B.S.763 : 1937 (sampling) B.S.735 : 1944 B.S.1017 : 1942 B.S.1016 : 1942
Concrete — —	Methods of Test (sampling materials and mixes) Precast blocks Ready-mixed	B.S.1881 : 1952 (6 in. cube, 6 in. diam. core or 14 lb. min.)* B.S.2028 : 1953 B.S.1926 : 1953 (sampling) (56 lb. min.)*
Creosote —	Coal tar Coal tar liquid fuels	B.S.144 : 1954 (1 gal. min.)* B.S.1469 : 1948 (1 gal. min.)*
Dust	Extraction, flues, power stations, etc. (methods of test and preparation of samples)	B.S.893 : 1940

MATERIALS	TYPE OR PURPOSE	REFERENCES
Ether	Solvent, technical	B.S.579:1957 ($\frac{1}{4}$ W.Qt.)*
Fillers	Miscellaneous (natural and synthetic)	B.S.812 : 1960 (7 lb. min.)*
Lime	Building	B.S.890 : 1940 (14 lb. min.)*
Media	Biological percolating filters (crushed stone, gravel, clin- ker, coke, slag, etc.)	B.S.1438 : 1948 (56 lb. min.)*
Naphthas	Coal-tar	B.S.479 : 1953 (1 gal. min.)*
Oil	Petroleum (crude)	(2 gal. min.)*
Perchloroethylene	Solvent	B.S.1593:1950 (1 gal. min.)*
Petroleum and allied products	Fuels, solvents	(1 gal. min.)*
Pitch	Natural or synthetic	(14 lb. min.)*
Pitch Mastic	Flooring, black	B.S.1450 : 1948 (12 in. sq. min. or 14 lb.)*
	Flooring (with lake asphalt)	B.S.1177 : 1944 (12 in. sq. min. or 14 lb.)* (obsolete)
	Flooring, coloured	B.S.1375 : 1947 (12 in. sq. min. or 14 lb.)*
	Flooring, coloured, (with lake asphalt)	B.S.1783 : 1951 (12 in. sq. min. or 14 lb.)*
Phenol	Miscellaneous	B.S.523 : 1955 (sampling) (1 gal. min.)*
Pigments	Colouring asphalt, cement, concrete, etc.	B.S.1014 : 1942 (7 lb. min.)*
Refractories	Miscellaneous	B.S.1902 : 1952 (Sampling depends on type and purpose of test).
Rocks (consolidated)	All types: chemical analyses, physical tests, petrological, mechanical, etc.	(6 lumps, each roughly 4 in. cube min.)*

MATERIALS	TYPE OR PURPOSE	REFERENCES
Rocks (incoherent)	All types: chemical analyses, physical tests, petrological, mechanical, etc.	B.S.63 : 1951 B.S.812 : 1960 (samples according to grade-size)
Sand	Miscellaneous	B.S.812 : 1960 (7 lb. min.)*
Sands	Building	B.S.882, 1201 : 1954 (7 lb. min.)*
Slag	Aggregate for concrete (applicable to asphalt)	B.S.1047 : 1952 (56 lb. min.)*
Slate	Roofing	B.S.680 : 1944
Soil	Methods of test	B.S.1377 : 1948 (1 cwt. min.)*
—	Methods of test (stabilized)	B.S.1924 : 1957 B.S.1377 : 1948 (1 cwt. min.)*
Tar	Road Purposes	B.S.76 : 1943 (1 gal. min.)*
—	Coal and products	B.S.616 : 1938 (1 gal. min.)*
Tarmacadam	Tar carpets	B.S.802 : 1958 (spec.) B.S.598 : 1958 (sampling) (Size of sample varies with grade-size of aggregate)
—	Tar carpets (gravel aggregate)	B.S.1241 : 1959 (spec.) B.S.598 : 1958 (sampling) (Size of sample varies with grade-size of aggregate)
—	Tar paving	B.S.1242 : 1945 (spec.) B.S.598 : 1958 (sampling)
Trichloroethylene	Solvent, degreaser	B.S.580 : 1950 (1 gal. min.)*
Toluoles	Solvent	B.S.805 : 1953 (1 gal. min.)*
Water	Potable, industrial	E. W. Taylor (Thresh- Beale-Suckling). Examination of Waters, etc. 6th ed., 1949, ch.13. (1 W.Qt.)*
—	Steam generation	B.S.1328 : 1956 (sampling)
Xyoles	Solvent	B.S.458 : 1953 (1 gal. min.)*

CHAPTER III

LABORATORY TECHNIQUE

PART I—PREPARATORY METHODS

Dry Samples—Megascopic (Macroscopic) Examination—Thin Section Preparation—Schedule of Equipment—Rock-Cutting and Grinding (Mechanical)—Rock-Splitting and Crushing—Polishing—Mechanized Fossil Extraction—Points in the Preparation and Mounting of Friable and Impregnated Rocks for Thin Section Examination—Mounts other than with Canada Balsam—Impregnating Friable and Porous Rocks—Conventional Thickness of Rock-Sections—Treatment of Incoherent Rocks for Recovery of Heavy Minerals, Micro-Organisms, etc.—Single Heavy Mineral Separations—Heavy Residue Sampling—Mounting of Sand Grains for Microscopical Examination—Systematic Procedure for Simultaneous Investigation of Samples for Micro-Organisms and Heavy Minerals—Special Methods of Concentration: Panning—Centrifugal Methods—Heavy Liquids and Substances other than Bromoform for Mineral Separation—Detrital Mineral Concentration by Hand—Elimination of Prolific Minerals from Heavy Residues—Treatment of Argillaceous Rocks—Treatment of Calcareous Rocks—Treatment of Carbonaceous Rocks—Treatment of Bituminous Impregnated Rocks—Treatment of Crushed Rocks for Heavy Mineral Separation.

DRY SAMPLES

SEDIMENTARY (incoherent) rock-samples should be thoroughly dried before examination. Oil-well samples are generally wet and in this state are apt to prove misleading in diagnosis, particularly if any oil is present. Where a number of samples is being constantly handled, the most convenient and satisfactory means of drying them is on a long rectangular iron plate, about $\frac{1}{4}$ in. thick, suitably supported on tripod-stands and heated by bunsen gas-burners or, in the absence of gas supply, by ordinary oil-stoves; in the latter case the iron plate may be supported on trestles with pieces of asbestos inserted between the wood and the iron. The samples are emptied from their containers, spread out on square-cut pieces of paper or filter papers of suitable size, placed on the plate and thus

left to dry. Care should be taken not to overheat the plate and char the paper.

MEGASCOPIC (MACROSCOPIC) EXAMINATION

Prior to special treatment for detailed analysis, the maximum information should be obtained from samples by eye-inspection, aided with a hand-lens and also with a binocular microscope, if available and where relevant (p. 212), such information being recorded at the outset on the appropriate index-card (p. 70) or in a sample record-book.

The following are the chief points of observation:

- a. Identification.
- b. Colour.
- c. Texture.
- d. Composition (inorganic constituents).
- e. Fossils or organic structures.
- f. Bedding, lamination, cleavage, etc.
- g. Special structures or characteristics.

a. Specific identity may not always be possible without recourse to thin sections or special tests (p. 111). The chief difficulties arise with compact, fine-grained rocks, *e.g.*, limestone, marl, salt, anhydrite, gypsum, while different coloured shale or mudstone fragments may simulate other types. Knowledge of what to expect from any particular horizon may help, but doubtful cases should always be subjected to exhaustive investigation before 'labels' are applied with confidence.

b. Colour varies markedly in sediments according to whether the samples are wet or dry. Frequently the former state aids diagnosis, but inherent colour must be determined in the dry rock. There are standard colour-systems in use by some petrologists, *e.g.* Munsell, Ridgway¹, and N.R.C.C.S.² schemes, which are sometimes useful for comparative purposes. Note should be taken as to whether the colour is due to particular ingredients, whether it is superficial stain or tarnish, a weathering product or inherent to the rock as a whole.

c. The coarse, medium, or fine texture of a rock should express relationship to its actual mechanical analysis, but, short of quantitative data, the terms are purely comparative. Experience of varied sedimentary rock-types and an 'eye' for grade-size of components, however, enables the observer to use these terms more or less accurately. Texture should apply as an average to the specimen as a whole, but may, of course, be restricted to cementing material independently of the large constituents, *e.g.* conglomerate with $\frac{1}{2}$ in. pebbles set in a *fine* compact matrix. The cult of 'textural analysis', as it is called, stemmed largely from intensive researches into grain-size of sedimentary rocks in the

¹ R. Ridgway, *Colour Standards and Colour Nomenclature*, 1912.

² National Research Council, Committee on Sedimentation (U.S.A.); Colour-Chart obtainable from headquarters, Washington (D.C.).

U.S.A. before the Second World War; it is now an established technique in this petrography; as a quantitative estimation, its consideration is deferred to a subsequent chapter (IV). Qualitatively, clay, marl, siltstone (components 0.1 mm.) imply fineness of texture, individual particles being practically invisible to the unaided eye in the case of siltstone, entirely so in the argillaceous types. Normal sandstones, grits and the like, frequently approximate size-limits 0.25 mm. to 0.5 mm., and are thus correctly labelled 'of medium texture'. Above the larger dimension, the particles assume characters which tend to guide the observer to the correct definition 'coarse', especially 1 mm. and 2 mm. particles, while the presence of pebbles automatically leads to this description unless the matrix alone is considered (*supra*). Limestones devoid of visible organic remains are usually of the compact, fine-textured type; so-called 'shelly' limestones approximate the coarser rocks; oolitic types vary from medium to coarse texture, pisolitic varieties invariably coming under the latter category. *Shape does not affect the question of texture.* Texture has some bearing on 'tightness' or 'openness' of rocks acting as oil-containers, though it must be remembered that it is not alone an indication of porosity or permeability.

d. Composition (inorganic constituents) is essentially a record of lithology of the sediment and implies recognition of those features characteristic of particular rock-types, e.g. sandstone, grit, arkose, quartzite, shale, marl, limestone, etc. Naturally it also implies the mineralogy of the sediment in so far as this is determinable without microscopic aid. In the coarser rocks the shape of the prominent constituents, angular, subangular or rounded, comes into consideration, especially where pebbles are concerned (p. 290), but in a majority of cases 'shape' of particles is more accurately recorded under the microscope (p. 230). Other points to note under this heading are surface characters dependent on weathering (if any), uniformity or heterogeneity of components and any unusual lithologic features.

e. Fossils or organic structures, whether determinable or not, should be recorded as such when occurring in the rock. Obviously, if determinable, the rock becomes distinctive at once; if not, even the presence of organic remains, either vegetable or animal, is of some diagnostic value. There is seldom difficulty in recognizing constituents as organic remains, even if they are not sufficiently well preserved to afford clues to their precise nature and origin; a hand-lens is always effective in this connexion. Some distinction should be made between dominantly fossiliferous rocks, those which are only partly fossiliferous and those of which the organic remains are few and far between. The orientation of the organisms should also be noted. The nature of the petrification is important; it may be calcareous, siliceous, pyritous, phosphatic, limonitic, more rarely other minerals. The calcareous forms include calcite and aragonite preservation; in the former category fall most of the vitreous forms of *foraminifera*, many sponges, corals, echinoderms, polyzoans, brachiopods, etc.; lamellibranchs consist mainly of aragonite (except the common *Ostrea* and *Pecten*), as also do gastropods

(excluding some species of *Fusinus*), porcellaneous forms of *foraminifera* and cephalopods (ammonites frequently show much secondary calcite and pyrite); in crustaceans the shell usually consists of chitinous material, calcite and phosphate of lime¹. Where only casts or impressions of the organisms are seen, the nature of these should be carefully ascertained and, if desired, wax or plaster moulds taken. Note the significance of the presence of glauconite in association with organic remains.

f. Distinction should at once be drawn between specimens exhibiting bedding or lamination, cleavage, or any linear or curvilinear structures and those devoid of same. Note whether the bedding, if developed, is uniform or variable, thin or thick, regular or cross (current-bedding); whether shaly-lamination is apparent or not; whether the bedding-surface is smooth, flat, crumpled or rippled and, if the latter, the nature of the marking (symmetrical or asymmetrical); cleavage, though it may be clearly apparent to megascopic observation, is better studied in thin section, especially in its relationship to reconstituted minerals etc.

g. Special structures or characteristics are those which tend to give individuality to any particular rock-type, such as surface-markings, mud-cracks, rain-prints, worm-tubes, -tracks, -impressions, mineral 'spots', peculiar modes of weathering, minute warping and shear-structures, angular jointing (with bedding or cleavage), secondary mineral developments as veins, blebs, cavities, bituminous impregnations, distinctive constituents, etc.: in short, any feature which, by its conspicuous and possibly widespread development, tends to individualize the rock and thus render its identification and history easy of interpretation.

THIN SECTION PREPARATION²

Methods of thin section preparation are now so generally known as to have become almost universally standardized. It may be observed at outset that in general sedimentary rocks demand a greater degree of skill in the manufacture of really thin slices than igneous rocks owing to their inherently softer and more friable character; in fact, many sedimentary rocks demand special treatment and technique before sections can be made from them at all; such departures from normal routine are discussed in the sequel (p. 91).

It must also be borne in mind that field-laboratories are not usually equipped with elaborate rock-cutting machines and that hammered fragments from outcrop specimens or, as is more common, well-sample chips or core-flakes, constitute the only available raw materials. It requires considerable experience and skill, for instance, to take bailer cuttings of, say, $\frac{1}{4}$ in. diameter (perhaps

¹ H. Woods, *Palaeontology*, 8th ed., (University Press, Cambridge), 1947.

² H. B. Milner and G. M. Part, *Methods in Practical Petrology*, (Heffer, Cambridge), 1916.

the largest pieces available of a critical rock-horizon penetrated) and produce therefrom satisfactory slices which will respond to the most refined optical examination; however, it can be, and often is, done with remarkable consistency by lapidaries who really know their work.

SCHEDULE OF EQUIPMENT

While it is freely admitted that individual taste and experience play a large part in selection of appropriate apparatus for this work, the author has found from long experience that the following equipment is most economical and satisfactory for all field-laboratory purposes, or for those operations where neither personnel, time nor money is available for large-scale procedure and output:

- Steel Plate (machined) for coarse grinding, circular, 12 in. \times $\frac{1}{4}$ in. or $\frac{3}{8}$ in., alternatively square, 12 in. \times 12 in. \times $\frac{3}{8}$ in.
- Glass Plates with ground edges, square, 12 in. \times 12 in. \times $\frac{3}{8}$ in. for medium and fine grindings.
- Wooden Trays (3), preferably teak (essential wood for tropics) to accommodate above plates, 13 $\frac{1}{2}$ in. \times 13 $\frac{1}{2}$ in. \times 1 in. deep (inside dimensions).
- *Copper Plate (hard drawn) about 15 in. \times 4 $\frac{1}{2}$ in. \times $\frac{3}{8}$ in. for heating balsam on glass slips, to accommodate 12 at a time.
- *Tripod Stands (2) to hold copper plate, 8 in. or 10 in. high, depending on burner used.
- *Microscope Slips, clear glass, ground edges, 3 in. \times 1 in., 0.75 mm. to 1 mm. thick (supplied by the gross).
- *Cover Glasses, No. 1 quality, rectangular, $\frac{7}{8}$ in. \times $\frac{7}{8}$ in. (Approximately 1 oz. per gross of slides.)
- *Forceps, stainless steel or nickel plated, with ribs and fine points, 10 cm. long.
- *Soft Toothbrush for removing surplus balsam in methylated spirits.
- *Photographic Developing Dish ($\frac{1}{2}$ -plate size) or large Evaporating Basin for cleaning slides.
- *Canada Balsam (*filtered*, not solution in Xylol) in 1 lb. bottles (coloured glass).
- Carborundum: grit 90 for coarse grinding, grit 220 for medium grinding, minute powder 60 mm. for fine grinding.
- Emery Powder FFFF for fine grinding and special work.
- Putty or Rouge Powder for polishing rock-surfaces.
- Shellac Flakes for 'cooking' friable or soft rocks (mix 2 parts of balsam and 1 part shellac).
- Bakelite Cement for friable rocks (p. 94).
- *Methylated Spirits, Benzol or Xylol for removing surplus balsam (the first recommended for preference).
- Glycerine for special 'dry' grinding.

* N.B. These materials are also used in the mounting of incoherent sediments, heavy mineral residues and the like. When indenting for

the above equipment, quantities should be ordered which are commensurate with the work in view and with the facilities available for replenishment of supplies as materials become exhausted.

If some form of rock-cutting machine is employed (p. 88), add to the above list the following items as may be required:

Spare cutting discs.

Extra supply of coarse carborundum.

Diamond Dust ('Diamond Splint').

Flint Pebbles for bedding diamond dust in cutting-disc edge.

Thin lubricating oil, paraffin or cutting oil.

The following procedure applies to normal hard rocks, whether igneous, sedimentary or metamorphic and to manual preparation of thin sections. The fragment is first ground down with coarse carborundum mixed with water on the steel plate until as large an area as possible, of uniform surface, is obtained. It is then washed free of carborundum and transferred to the medium (glass) plate, where a similar grinding with medium carborundum reduces the surface still further, removing all scratches etc., due to the coarse grinding and preparing the flake for the next grinding on the fine plate, using 'minute powder' or emery as detailed above. The utmost care should be taken to see that no coarse carborundum finds its way on to the medium plate and that no medium powder has access to the fine plate, otherwise the plates will soon be ruined, if not the slices under preparation; this possibility is easily avoided by careful washing under running water between each grinding and by keeping each of the trays some distance apart. After a satisfactory surface has resulted from the fine grinding (it should show no scratches or blemishes of any kind), the chip is well washed, then dried on a hot plate.

It is often found that with many sedimentary rocks the coarse abrasive is too drastic and a cautious use of the medium grit is all that is necessary to secure both rapid and successful results. In soft rocks it may only be practicable to grind steadily with minute powder or emery, whichever is preferred, if a reasonable-sized fragment is to be salvaged from disintegration. Much of this trouble can, however, be obviated by preliminary cooking of brittle or perforated rocks in the shellac-balsam mixture (above) for half an hour previous to grinding; use a can-lid on the hot plate for this purpose. In special cases it may be necessary to resort to dry grinding (p. 91) or to some form of resin impregnation (p. 94).

Once the rock-chip is dried after the first grindings, the next operation is that of mounting it on the glass slip and on this process the ultimate success of the work depends. First mark the bottom

end of the slip the reference number of the rock; this is done with a diamond and ensures that no mixing up of specimens occurs (where a number is being cut together). The rock-chip is mounted on the side of the slip *not* marked with the diamond. This obviates any danger of the reference number being removed in the subsequent grinding. Then proceed as follows: 'some balsam is spread on the glass slide and heated on the copper plate. It is sufficiently cooked when a thread drawn out between the points of a pair of forceps becomes brittle when cold. *Insufficiently cooked balsam will absorb carborundum during the second grinding. Overcooked balsam is too brittle and will break away, thus exposing the edges of the rock-chip which it is there to protect.* When the balsam is just right for mounting, the rock-chip, which has also been heating meanwhile, is placed, polished surface downwards, on the slip and firmly pressed down, care being taken to exclude air-bubbles. If any of these remain, the slip must be reheated and the chip worked about until the bubbles are pressed out. When cold, the second grinding may be proceeded with¹.

When thoroughly cold and firm, the chip is ground down once again on the coarse plate, if it initially stood this abrasive, until it is about 1 mm. thick, the glass slip being used as a convenient holder. The surface attained, it is washed and transferred to the medium plate where further grinding with the 220 grit reduces the chip to a state of translucency. It is washed again and finished on the fine plate. If during the final grindings balsam tends to come away from the rock, either transfer the latter to a new slip on which a fresh supply of balsam has been cooked in readiness, or pour suitably cooked balsam on to the specimen so as to surround the exposed edges completely and allow to harden.

In the final stages of grinding on the fine plate, great care must be taken to avoid unequal pressure on different parts of the slice; if there is a tendency to thickness in any particular area of the slice, it may be checked by grinding that part on the edge of the plate until uniformity of surface is obtained. Check the progress of operations with the microscope carefully and often, using crossed nicols to ascertain thickness (p. 233).

When the slice is of requisite thinness, dry cautiously on the hot plate until all moisture is driven off. In the case of normal hard rocks, fresh balsam may be placed on the dried chip, slowly cooked to the right degree and then covered with the cover-glass on which a thin coating of balsam has also been allowed to cook. With soft rocks it is advisable to cook the fresh balsam on a separate slip and then to pour it on to the dried slice, following this operation at once by placing the cover-glass in position as in the first case.

¹ H. B. Milner and G. M. Part, *op. cit.*, p. 9.

Air-bubbles are expelled by gentle pressure with the forceps on the cover-glass while the balsam is in a fluid state.

An alternative, neater and more skilful procedure is to transfer the finished slice to a new glass slip on which adequately cooked balsam is ready to receive it. With hard compact rocks, this may not present great difficulty, but with softer, coarse-textured examples it is a different matter altogether. In fact it may be said that the skill of a lapidary is directly proportional to ability to achieve successful transfers with almost all rock types.

The best way to proceed in transferring is as follows: on to the finished dry and cold slice on the original glass slip, pour enough properly cooked balsam to cover same and place the slip alongside a new glass slip (also with properly cooked balsam) so that their long edges coincide and the balsam from each amalgamates. When this happens, ease the rock-slice from the old on to the new slip in the balsam medium with the blunt point of forceps, then take the new mount off the hot plate and press the slice gently down to expel air bubbles. It is important in this procedure to see that there is no difference in thickness between the two glass slips in use, otherwise if there is a 'step-up' or 'down', the slice will inevitably break during transfer.

Sometimes it is possible to vary this procedure by holding the original slip with the rock slice over the hot plate at an inclined angle to the new slip and as the slice gets warm gently sliding it down into the cooked balsam on the new slip ready to receive it.

The final operation is to clean the slide. With the cover-glass in position and the air-bubbles expelled, the slide is allowed to cool and then all surplus balsam adhering to the edges of the slip is cleaned off with a soft toothbrush in methylated spirits. The cleaning process may be accelerated in skilful hands by flaking the solid balsam with a sharp knife, then cleaning with xylol or methylated spirit, but care must be taken to see that the cover-glass is not damaged in the process; also that the solvent does not dissolve the balsam from beneath the cover-glass. When clean, polish the slide with wash-leather and label with $\frac{3}{4}$ in. square labels at each end. In this connexion it should be remembered that gummed labels may perish or become detached in the tropics; in such cases grind each end of the slide on the coarse plate until opaque, if this is not already achieved, and print the description of the slide with Indian ink on the surface thus produced. Alternatively, an identity mark or number can be scratched on the slide with a diamond, or etched with hydrofluoric acid on a wax-covered area, the wax being suitably incised with a fine wire point; this last, however, is a tedious and not very satisfactory procedure.

ROCK-CUTTING AND GRINDING (MECHANICAL)

In most established petrological departments of Universities, Technical Colleges and Industrial Works, concerned with 'mass' thin-section production, some form of mechanically-operated rock-cutting and now, especially, grinding apparatus, is an essential part of the permanent equipment. Rock-cutting *per se* has, of course, always implied a machine to do the work. The pattern has evolved with the years from a somewhat crude, treadle-operated horizontally mounted and rotated, mild steel cutting disc, via the vertically mounted type¹, to the more modern bench rock-cutter or combined cutting and grinding machine. In the early part of the century, diamond-loaded cutting discs were exception rather than rule, carborundum being fed (wet) to the disc as it revolved within the rock during slitting. Nowadays, diamond-loaded discs are almost universal and the rock-cutter has become a precision machine.

Probably the most efficient unit of modern design is the combined high-speed cutting and grinding machine referred to above, of which there are both vertically- and horizontally-mounted cutting disc versions. One such apparatus (Pl. I) 'incorporates three electric motors driving the cutting disc, grinding disc, and coolant supply, respectively, and is totally encased with all starters built in. The cutting disc is a 12 in. diameter diamond-impregnated wheel and the grinding disc employed can be either a 4 in. or 6 in. diameter fine-grade diamond wheel'². Semi-portable, bench-mounted machines, using 8 in. diameter diamond-impregnated discs, are also available.

Into the range of rock-cutting machines has also been recently introduced apparatus for cutting longitudinal or cross-sections from circular cores up to 5 in. in diameter; cube-cutting machines capable of producing accurate cubes from rough hand-specimens; also prisms of any number of sides and angles³. Thus the lapidary concerned with routine petrographic work in the laboratory is now in a position to turn out thin sections and dimensional specimens for mechanical tests, polished exhibits, etc., with far greater speed and less fatigue than earlier workers in this field.

On a much larger scale, stone-working machinery such as is employed by ornamental masons in fashioning polished granite, limestone, marble, etc., is available for quite a range of requirements in the technical field, e.g. 1 in. × 1 in. diameter cylinders for mechanical tests (B.S.812 : 1960); 6 in. cubes of concrete; slabs of marble (e.g. Purbeck limestone) for decorative purposes, and so on.

¹ H. B. Milner and G. M. Part, *op. cit.*, pp. 4, 6.

^{2,3} Cutrock Engineering Co., Ltd., London. N.3

In fact, in circumstances where a problem in rock-cutting cannot be solved by the laboratory machine, a stone-masons' works will usually supply the answer.

ROCK-SPLITTING AND CRUSHING

There are many ways of dividing a solid rock-specimen into two or more parts, by hammer (with or without cold steel chisel) plus brute force or by some form of machine designed specially for the job. A modern type of the latter is the hydraulic rock-splitting and crushing machine¹, consisting essentially of two hardened-steel splitting jaws within which the specimen is placed in contact top and bottom. Pumping by means of a hydraulic jack, at 6–8-ton pressure, eventually splits it. The crushing attachment is fitted above the jaws of the machine and a piston operates in a chamber in which the rock is placed. Crushing pressure is exerted by the hydraulic jack and after the necessary pressure applications have been made, complete pulverization of the specimen is achieved.

In circumstances where apparatus for testing in compression at relatively high pressures is installed, *e.g.* 1 in. diameter and 1 in. high cylinders cut from rocks for crushing strength² or concrete cubes or cores, both rock-splitting and especially crushing, are easily carried out rapidly and efficiently.

POLISHING

Examination of polished surfaces of metalliferous ores by reflected light using a metallurgical microscope is a well-ordered technique in determination of natural ore-minerals and of crystalline structures in various metals. It is not, however, a process commonly employed with sedimentary rocks *per se*. The part polishing plays in assessing certain slag aggregate qualities is described in B.S. 1047. The polished surface method has also been successfully applied to certain coals³.

In so far as rocks, ore and opaque minerals are concerned, to achieve a highly polished surface for diagnostic work simply involves the conventional method of grinding to flat surface, thereafter polishing with selected media, usually on some form of textile-covered plate or lapping machine⁴. The long-established local Cornish industry in making and polishing articles from serpentine is a good introduction to polishing rock-surfaces and although

¹ Cutrock Engineering Co., Ltd., London, N.3.

² B.S.812 : 1960, clause 32.

³ W. H. Twenhofel and S. A. Tyler, *Methods of Study of Sediments* (McGraw Hill, New York and London), 1941, p. 157 and refs. cited.

⁴ Cutrock Engineering Co., Ltd., London, N.3.

sometimes rather crudely performed, is none the less effective. Of the media used alundum, rouge, magnesia, ferric oxide, chromic oxide, are among the commonest, while the cloth laps vary from fine muslin to billiard cloth or chamois leather. For detailed references see below¹.

MECHANIZED FOSSIL EXTRACTION

To the practical palaeontologist often falls the task, in the course of his investigations, of extracting without any damage whatsoever, whole fossil remains from their mother rock. Sometimes this is a comparatively simple matter depending on state of preservation and nature both of fossil and rock concerned, and cautious work with small hammer and chisel has the desired effect. In soft, relatively unconsolidated strata, other implements, e.g. knife, scalpel, may be employed with advantage. Where, however, delicate shell remains are to be released from the enclosing rock, especially when internal structures are to be exposed without injury, then certain specialized laboratory facilities must be available.

An instance of this sort of technique is the cleaning out of certain chalk *brachiopoda* in the interior of the valves to expose intact the brachial skeleton of the species under examination. This operation requires a considerable degree of skill, especially if manually performed. The whole process is, however, greatly facilitated by using a high-speed portable electric drill which, with appropriate hardened steel, small diameter (e.g. $\frac{1}{16}$ in.) cutting or grinding 'bits', can be guided through the intricacies of the skeletal remains in such a manner as to remove the rock without harming the organism. The ordinary dentists' drill, shorn of its complicated accessories, is another type of instrument involved and in its simplified form (either foot or electrically operated) has been successfully adapted for the purpose in many palaeontological laboratories.

The modern version, however, is the precision, miniature machine tool drill, operating electrically at high speed, and so 'cabled' as to give great freedom of operation in the most difficult places encountered in the fossil specimen concerned. The efficiency and success of this procedure naturally hinge on the degree of hardness of the rock-type involved, but even tough limestones are sometimes susceptible of treatment in this way, while sandstones, slates, shales and coals are relatively straightforward materials to work upon.

Normal process is to clamp the specimen in convenient position; mark out the periphery of the fossil to be extracted, allowing a good

¹ G. C. Kennedy, The Preparation of Polished Thin Sections, *Econ. Geol.*, **40**, 1945, p. 353. M. N. Short, Microscopic Determination of the Ore Minerals, *Bull. U.S. Geol. Surv.*, 914, 1940.

margin between it and the cutting line; then proceed to 'drill up' at close intervals round the line to a depth in the rock commensurate with the dimensions of the organism to be extracted. Thereafter, with cautious aid of both drill and accessory tools, such as a small geological hammer and chisel, removal of the fossil without injury, is just a matter of patience and time. The variations possible on this technique are almost infinite in skilled hands, but it must be admitted that wear and tear on bits with hard rocks is considerable. Use a cutting oil lubricant in difficult cases.

From the purely petrological standpoint, a similar procedure is often effective in isolation of specific components from sedimentary rocks other than siliceous; the latter require diamond-loaded bits for successful attack; it is generally more practical to use a rock-cutting machine with such hard types.

POINTS IN THE PREPARATION AND MOUNTING OF FRIABLE AND IMPREGNATED ROCKS FOR THIN SECTION EXAMINATION

Those who have had experience of producing thin sections of friable rocks or bituminous impregnated sediments are aware of some of the difficulties occasioned by these types; the tendency of the former to crumble or disintegrate, if not in the early stages of grinding, often just before the section is achieved, and the trouble caused by fluxing of the bitumen when mounting with warm Canada balsam in the case of the latter, are familiar troubles to be overcome. In these connexions, the late E. J. Tallin of the Geological Department, Imperial College of Science and Technology (to whose skilful preparations of thin sections of such rocks the author has on many occasions been indebted in the past), contributed the following brief account of his own technique:

'Before proceeding with the usual grinding of such rocks as clays, shales, some limestones, certain loosely cemented sandstones, lignitic material, schist and any weathered or much-altered rock, the slice to be sectioned should be thoroughly warmed to get rid of any moisture present. It should then be immersed in a bath of Canada balsam and cooked until this medium is tough but not brittle, just hard enough, in fact, to be impressionable with the finger-nail. When quite cool, the grinding of the slice may be proceeded with in the usual way.

'The above method is not applicable to bituminous rocks since in these cases slight warming causes the bitumen to migrate, either leaking out altogether, saturating parts of the rock not previously saturated, or fluxing with the Canada balsam. The effect of such movement is likely to give an erroneous impression of the impregnation when the section is examined under the microscope. Also, many of these rocks on

warming become warped, even corrugated, thus preventing the achievement of a uniformly thin section. Again, certain constituents of oil-bearing rocks are soluble in water, hence these are lost if the ordinary methods of preparation are adopted.

'Dry cutting such rocks is therefore advisable, the cutting disc being lubricated with a little glycerine. The slice thus obtained is carefully ground on a metal plate with 3F carborundum, then with washed flour emery, and lastly on a Water of Ayr Stone, using glycerine as before. Canada balsam used for mounting the slice is previously cooked before it is poured on to the glass slip, and the slice must be quite dry before it is mounted. The second grinding is carried out on a carborundum cloth (grit 90) fastened down to a flat surface, and is proceeded with until the slice is flush with the surface of the balsam. The back of the glass slip should be periodically examined for 'flaking', *i.e.* fracture of contact between the slice and the slip. Final grinding is carried out on fine carborundum cloth; in some cases this is too drastic, when gentle rubbing on a selvyt cloth may be tried; this procedure is, however, very slow. When the slice is of the requisite thinness, it is dried and covered with a cover-glass on which sufficient balsam has previously been cooked; this avoids warming the section more than necessary, and in this way the slide is completed.

'With very soft or plastic rocks, the use of a razor blade or even a microtome may prove more satisfactory than trying to grind down sections in the usual way.'

MOUNTS OTHER THAN WITH CANADA BALSAM

The great advantage of mounting in Canada balsam is the refractive index standard it provides for subsequent optical determinations of the rock-minerals. This value (cooked balsam 1.538) approximates that of quartz, frequently used as the index-mineral of thickness (or required thinness) of section. There are cases, however, where it is not possible to use Canada balsam, especially if there is anything in the rock which easily fluxes with this medium on slight heat application (*e.g.* certain types of bitumen) or where, owing to the inherent nature of the rock, it is not possible to impregnate with balsam-shellac or synthetic resin (p. 94). Canada balsam solution in xylol or other solvent is unsatisfactory except for purely temporary mounts since, when the solvent has evaporated, it takes a long time for the balsam to dry; in hot weather or tropical places, it may remain 'tacky' indefinitely, to the discomfort both of the operator and microscope.

In difficult cases, air-mounting may be resorted to, the slice having been dry or semi-wet ground previously, taken as thin as possible, thoroughly dried, thereafter transferred to a dry, clean and *thin* glass slip. The refractive index of air being 1, it follows that the normal R.I. standards of comparison of rock-minerals are

completely altered. In point of fact, quartz (1.550) appears in strong relief in contrast to its normal demeanour in Canada balsam. Where a slice is air-mounted, the edges of the cover slip must be sealed either with wax or with a solution of bitumen in benzol; this is done by painting round the cover slip with a fine camel-hair brush dipped in the solution.

Various forms of wax are also used successfully as mountants, from ordinary paraffin wax to specially prepared, so-called 'Sira' wax, the latter useful where tenacity combined with a certain degree of plasticity is required.

Synthetic resins are applied more particularly to impregnating friable and porous rocks to enable them to be mounted with balsam; these resins are seldom used as mountants *per se*, though in special cases they may be appropriate. Their average R.I. is 1.62 (after heat treatment).

Pure rubber dissolved in xylene is sometimes used as a mounting medium in the microscopical examination of fine powders, *e.g.* pigments in the paint industry. It has a refractive index of 1.517 and forms a rigid bond, though it may not be optically clear.

As a temporary mounting medium, gelatine solution is much favoured in industrial microscopy, especially where extremely fine particles and colloidal materials tending to exhibit Brownian movement are involved¹. Such a solution is prepared by dissolving 7 g. of best emulsion gelatine in 100 ml. of distilled water to which 1 ml. carbolic acid solution is added (to prevent mould developing). When the gelatine is dissolved, a little albumen is added and the solution separated from the 'foam', placed over a boiling water bath for half an hour and the clean gelatine then removed. The resulting solution is optically clear and can be used with advantage in many cases when investigating clay particles, fillers and the like.

W. Ahrens and H. Weyland² have recommended methylene methylethylketone as a mounting medium, the R.I. being 1.519 to 1.520.

T. W. Parker and R. W. Nurse³ have employed bromoform as a mountant in connexion with determination of percentage glass in granulated blastfurnace slag. Their method is to take about 5 g. slag sample all passing 100 B.S. sieve. From this is extracted the — 170 + 300 B.S. sieve material. 'A few milligrams of the material are mounted on a microscope slide in bromoform and examined by transmitted light at a magnification of $\times 200$, using an eyepiece

¹ C. H. Butcher, *Ind. Chem.*, 9, 1933, p. 296.

² *Centr. f. Min.*, 1928, p. 370.

³ Investigations on Granulated Blastfurnace Slags for the Manufacture of Portland Blastfurnace Cement, Nat. Building Studies, *Tech. Paper*, No. 3. D.S.I.R., London, 1949, p. 18.

with a graticule. The total number of grains in the field is counted, and also the number of these which are substantially opaque. The latter is then expressed as a percentage of the former and subtracted from 100 to obtain the percentage glass.' This method has been employed successfully in the author's laboratories.

IMPREGNATING FRIABLE AND POROUS ROCKS—THE USE OF SYNTHETIC RESIN

The essence of the use of resin for rock-sections is its ability to be introduced in liquid form and thereafter by heat treatment converted to a hard solid without deforming or affecting the rock substance or structure in any way.

A. F. Hallimond employed this method in sectioning soft rocks such as clays and chamosite mudstones¹. C. S. Ross used 'Bakelite' resin in a similar way for friable materials and has also described a method of surface treatment using either synthetic resin or a medium known as 'Kollolith', a substance not unlike Canada balsam². A. Scott Russell, in his work in connexion with stone preservation, developed special methods for sectioning disintegrated building stones in which specially prepared synthetic resin was employed³. M. Leggette⁴ has used 'Bakelite' successfully with silts, clays, 'bentonite', etc., to preserve original structures when grinding these rocks. R. J. Schaffer and P. Hirst⁵ investigated these processes in the course of research on weathering of building stones and their methods as developed at the Building Research Station (Department of Scientific and Industrial Research) are now generally followed in this country.

A dyed synthetic resin of the phenol formaldehyde type is employed with considerable success for all types of soft and friable rocks, building materials, cements, refractories and similar subjects. Among the advantages of such resin over Canada balsam may be mentioned the following:

(a) Rocks impregnated with resin will stand grinding much better than those mounted with balsam.

(b) Sections impregnated with resin do not 'float' in the mounting process.

(c) Resin is easily dyed and when used in this form enables comparisons of porosities by detection of fissures to be carried out very easily.

¹ Iron Ores etc., *Mem. Geol. Surv., Special Rep. Mineral Resources Great Britain*, 29, 1925, p. 37; also *Summary of Progress*, 1923 (1924), p. 144.

² *Amer. Journ. Sci.*, Ser. 5, vii, 1924, p. 483.

³ Report of the Stone Preservation Committee, London, 1927, p. 7.

⁴ *Journ. Geol.*, 36, 1928, p. 549. ⁵ *Proc. Geol. Assoc.*, 41, 1930, p. 32.

A disadvantage attaching to the use of resin is that its refractive index, after baking, is approximately 1.62 as against 1.54 for cooked balsam and, therefore, the minerals in the slice mounted in resin have an abnormal appearance. With practice, however, this difficulty is soon overcome.

Two grades of resin are employed; a mixture of formaldehyde, phenol and m-cresol in the molecular proportions 6 : 3 : 3 is used for all normal purposes and a softer resin, prepared from a $5\frac{1}{2}$: 3 : 3 mix, for very friable specimens, particularly those which are badly weathered.

The preparation of these resins is as follows. A round-bottomed flask of 1,000 ml. capacity is weighed and the requisite amount of phenol, m-cresol and formaldehyde added, the latter in the form of 40% solution. To catalyse the reaction, 1.5 ml. of ammonia (sp.gr. 0.880) are added for each 100 ml. of formaldehyde solution, after which the flask is closed with a double-bored cork through which a small mercury manometer and a tube closed with a stop-cock are inserted. The flask is heated on a steam bath for several hours until the mixture turns permanently cloudy and does not clear again on shaking. During this period, the pressure in the flask is maintained at approximately atmospheric by opening the stop-cock at intervals. The mixture is then run from the flask into a separating funnel and, when cold, the resinous layer is transferred to another 1,000 ml. round-bottomed flask. Safranine, amounting to about 5% of the weight of the entire batch of resin, is added. For a paler colour, the amount of dye may be reduced. This resin is then dehydrated in vacuo at 20°C to 30°C until its refractive index reaches 1.590–1.591 for the 6 : 3 : 3 mixture and 1.596–1.597 for the $5\frac{1}{2}$: 3 : 3 mixture. Dehydration is carried out by connecting the flask through a T-piece with a mercury manometer and drying towers of calcium chloride and sulphuric acid. A three-way stop-cock is fitted between the flask and the first drying tower and enables the flask to be connected at will with the outside atmosphere. The last drying tower is connected with a vacuum pump and the apparatus evacuated to 12 mm. pressure, the flask containing the resin being immersed in water at 20°C to 30°C (Fig. 3).

Dehydration usually requires about 30 hours. If desired, the process may be stopped overnight, in which case air is admitted to the flask through the three-way tap before turning off the pump. This procedure avoids the possibility of sulphuric acid being forced back into the flask. Dehydration is considered to be complete when the refractive index of the resin as measured by a refractometer falls within the limits already given.

One of two processes is used for impregnation according to the nature of the work.

(a) *Surface Impregnation.* This method will be found to be adequate for all but the most delicate work. Material prepared as described above may be used or certain commercial grades of resin are equally

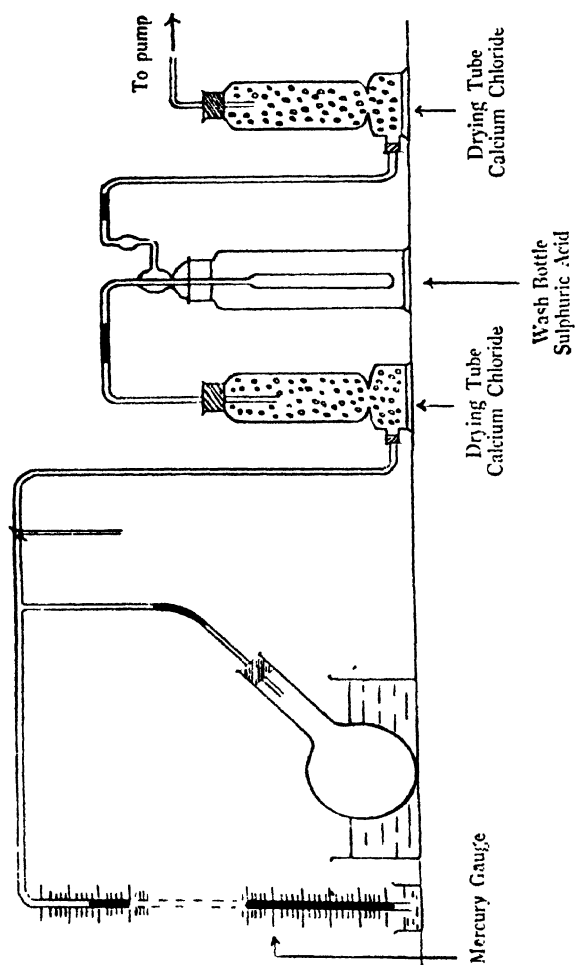


FIG. 3. Apparatus for Preparation of Synthetic Resin.



CUTROCK "MOTTACUITTA" SHOWING CUTTING AND GRINDING MECHANISMS.
(Courtesy Cutrock Engineering Co. Ltd., London, N 3)

suitable. If the resin as above is used with a solvent it should not be more than three weeks old. The section is cut to about $\frac{1}{8}$ in. in thickness and ground as flat as possible. It is then thoroughly dried and placed for a few minutes in an oven at 130°C , after which it is transferred to an electric hotplate, specially designed to give a uniform temperature of 115°C , and the resin applied in thin layers until no more is absorbed. This procedure minimizes the tendency to form air bubbles. The section is allowed to remain on the hotplate until it is quite hard while still hot, when it is taken off and ground on the medium and fine plates until the excess resin is just removed. The slice is then mounted in the normal manner except that, instead of placing it on the heated plate, it is warmed gently with a bunsen burner prior to laying it on the cooked balsam. In this way further contraction of the resin and dehydration of the material composing the slice is avoided. With comparatively non-porous materials, care must be taken not to grind too far, as in such specimens the actual depth to which the section is impregnated is comparatively small. An alternative method, which is very useful with some soft specimens, is to apply the resin in the form of an alcoholic solution with a brush and repeat as often as necessary, afterwards baking it at a temperature not exceeding 90°C . In this case the lower baking temperature causes hardening to occur more slowly and diminishes the possibility of setting up strains in the resin as a result of contraction taking place on solidification.

With comparatively robust specimens the method followed at the author's laboratories is to place the slices in a small beaker and cover with an alcoholic solution containing 30%–50% by weight of resin. The beaker is then gently warmed over a small flame until the bulk of the alcohol has evaporated and a viscous resin is left behind. During this process, the slices should occasionally be moved about with a glass rod to prevent them adhering to the bottom of the beaker. The amount of resin remaining at this stage should be more than sufficient to cover the slices. The slices are then removed and baked at a temperature not exceeding 90°C and the excess resin in the beaker diluted with alcohol and preserved for future use.

(b) *Thorough Impregnation.* This process is reserved for the most friable rocks and the resin used should be freshly made, since after 24 hours it becomes too viscous to be used for thorough impregnation. It is most economical therefore to reserve samples for thorough impregnation until a number has been collected. The size of the specimen required varies according to its nature; 2 in. \times 1 in. \times 1 in. is suitable for very fragile materials, the edges of which have to be preserved, and 1 in. \times 1 in. \times $\frac{1}{4}$ in. for those which are more robust. A flat tray capable of holding sufficient resin to cover the samples makes a suitable container for the purpose. When the

Sieves for coarse materials: see full list of B.S.I. medium-mesh test sieves and perforated plates, p. 165.

Evaporating Dishes, 16 cm. wide, shallow, porcelain, for cleaning sediments.

Glass Stirrers made from 5 mm. glass rod supplied in metre lengths by the 1 lb. weight.

Wire Gauze, iron, with asbestos combined, cut in 5 in. \times 5 in. squares for heating basins.

Tripod Stands, 8 in. or 10 in. high according to size of burners used.

Sand-Bath for drying acid-cleaned sediments.

24-Funnel-Battery for heavy liquid separations (as Fig. 6, p. 114).

Constructed of white wood or teak, $\frac{3}{4}$ in. or $\frac{1}{2}$ in. Overall length 4 ft. 6 in., width of base and shelves $10\frac{1}{2}$ in., each side $18\frac{1}{2}$ in. high, lower shelf $11\frac{1}{2}$ in. up from base, upper shelf $15\frac{1}{2}$ in. up from base, depth between shelves 4 in. Each shelf drilled with 24 holes, each 2 in. in diameter, one hole immediately behind the other, positions of holes in the lower shelf corresponding exactly with those in the upper shelf.

Retort Stand for holding funnels etc. (as Fig. 5, p. 103).

Funnels, white glass, short stem, 3 in. diameter.

Clock-Glasses to cover funnels, $3\frac{1}{2}$ in. diameter.

Rubber Tubing, black, $\frac{3}{8}$ in. diameter, supplied by the yard; $1\frac{1}{2}$ in. sufficient for each funnel.

Pinch-Grips, for rubber tubing.

Bottles, odd, coloured glass, for bromoform and solutions; also colourless for the funnel-battery, 24 to each.

Filter Papers, Whatman No. 41, 11 cm. diameter, supplied in boxes of 100 circles; fan-folded patterns to order.

Hydrometer as specification, p. 102.

Wash Bottle, 500 ml.

Hydrochloric Acid, commercial for cleaning, dilute 1 of acid with 4 of water.

Caustic Soda, solid, for making N/10 solution.

Bromoform, 2.9 sp.gr., in 5 lb. coloured glass bottles, carefully sealed and packed for export (where applicable).

Mercurous Nitrate, 4.3 sp.gr. as fused, in $\frac{1}{2}$ lb. bottles.

Benzol, pure, recrystallizable or 99% Industrial Methylated Spirits.

Methylene Iodide, 3.3 sp.gr., in 4 oz. bottles (coloured).

N.B.—Other 'heavy' liquids described on p. 119. See also schedule of equipment given on p. 84, items starred*.

For bromoform recovery from benzol etc., the following apparatus is desirable:

Engler-type Distillation Flask, 500 ml. capacity.

Liebig Condenser, glass body with inner tube fused in, 45 cm.

Condenser Stand, universal, with sliding rod and iron clamp.

Thermometer reading to 300°C.

Cork bored to take thermometer.

Wire Gauze and tripod stand as above.

SINGLE HEAVY MINERAL SEPARATIONS

The sample in the first place should be examined with a hand-lens for detection of the larger and more easily identifiable minerals or micro-organisms and for those which may be destroyed by subsequent treatment with acid; such minerals as pyrite, limonite and glauconite, together with carbonates and most phosphates, are included in this category. A little material should also be mounted dry on a glass slip and examined under the binocular microscope, both by transmitted and incident light. Use a 36-mesh B.S. sieve to segregate coarser constituents and operate on all material which passes this sieve. (For discussion of sieving etc., see p. 169.)

The authigenic material coating sand grains if present is removed by gently boiling with water; often this suffices, but in many cases addition of hydrochloric acid (1:4) is necessary to complete clarification, though with exceptionally ferruginous material, 1:1 hydrochloric acid may be necessary. It is, however, advisable to restrict as far as possible the quantity of acid used and also time of digestion, since partial destruction of certain minerals is inevitable and in some cases total decomposition or solution may follow, as indicated above; loss from this cause is anticipated by preliminary examination of the material as suggested. In the case of calcareous organisms, hydrochloric acid is obviously impracticable and use of a strong potassium or sodium hydroxide solution is suggested. This alkaline digest is also applicable with advantage to sediments, the limonitic content of which is not very great, though it takes longer time for clarification of grains than acid treatment; also to those cases where acid-soluble minerals are anticipated (as above). When the grains are clear they are washed free of acid or alkali with cold water and then dried slowly in a steam-oven or on a sand-bath.

The next operation involves the use of suitable 'heavy' liquids for concentrating either mineral particles having a sp.gr. greater than the arbitrary standard of 2.90, or micro-organisms which, if of calcite, have a sp.gr. of about 2.71, or silica particles of sp.gr. 2.59-2.65. For heavy minerals, of the many liquids advocated and in use, the author still favours bromoform (sp.gr. 2.88-2.90, varying considerably in purity) for all general purposes. The objections, that it is liable to excessive convection current effects, rapid evaporation, and that it is expensive to employ, may be met by certain preventive measures. These consist in carrying out the separation in a fume cupboard or constant temperature chamber, or in a room rendered free of air currents; also by keeping bromoform covered when in use with a watch-glass which fits the funnel and taking care to preserve benzol washings for ultimate recovery of bromoform dissolved. Further, the price of bromoform cannot be regarded as prohibitive

when compared with prices of the various other liquids sometimes employed. In the hands of a careful manipulator, 1 lb. of bromoform should be ample for separation of at least 50 samples, if care is taken to reduce loss to a minimum when recovering the liquid from benzol washings.

For calcite or calcareous organisms, dilute the bromoform with pure benzol (recrystallized) until the sp.gr. of the solution is 2.69 (test with a hydrometer). A solution of sp.gr. 2.45–2.50 will be effective in differentiating quartz and/or calcite from gypsum: the former species sink, the latter floats. Bromoform may thus be diluted to any strength, giving solutions of decreasing gravity and by this means specific minerals may be concentrated or diagnosed.

A type of hydrometer most suitable for checking the sp.gr. of bromoform and bromoform solutions is obtainable¹; it embodies the following essential features:

Length 20 cm.

Diameter of bulb 2 cm.

Range 2.6–3.0 (or other ranges as desired).

Scale graduated every 0.01 and made as long as possible so that graduations are clear.

Value 2.9 marked in red.

When testing the gravity of a solution, use a 500 ml. graduated glass vessel. Take care to insert the hydrometer cautiously; do not drop it into the liquid. In diluting bromoform, fill the vessel with sufficient liquid to float the hydrometer at 2.9, then carefully pour in benzol, stirring with a glass rod, until the desired gravity is registered. Both bromoform and bromoform solutions should be periodically checked for sp.gr., stored in coloured glass bottles, kept out of sunlight and *kept cool* (if possible in a refrigerator in hot countries). Deterioration is liable to be rapid if these precautions are not taken, especially if bromine starts to separate out. Should the liquid become badly discoloured, try shaking in a separating funnel with an aqueous solution of sodium hydroxide or an alcoholic solution of potassium hydroxide: the method may not be successful in bad cases of deterioration.

Redistillation is usually effective, but sometimes leads to a further settling out of bromine or hydrobromic acid. Recent trials employing distillation under reduced pressure have, however, given successful results.

Recovery of bromoform from benzol-bromoform solution (or benzol 'washings') is achieved by distillation, using an Engler-type flask, 500 ml. capacity and a Liebig condenser. Benzol boils at 80.5°C and comes over first; bromoform boils at 151.2°C; it is advisable to keep an eye on the condenser at the higher temperature

¹ Messrs. T. O. Blake (Silkes Hydrometers), Ltd., Belle Vue Terrace, London, N.W.4.

and stop circulation of cold water if large quantities of liquid are being distilled. S. Bracewell¹ advocates the use of methylated spirit instead of benzol for washing heavy mineral residues after bromoform separation. In this case the washings are poured into water;

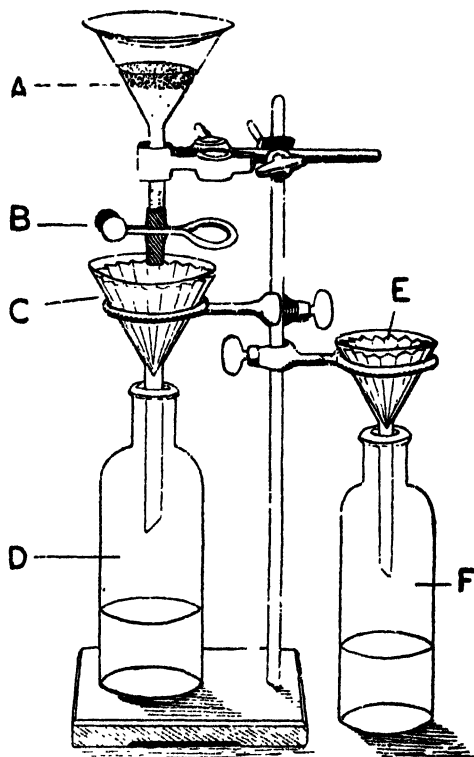


FIG. 5. Bromoform Separation Apparatus for Single Samples.

- A. Funnel containing bromoform and sample from which heavy grains are settling down.
- B. Pinch-cock grip on rubber tubing attached to funnel stem.
- C. Folded filter paper for holding up residue.
- D. Bromoform bottle.
- E. Filter to prevent any solid material from entering F.
- F. Benzol (or other solvent) washings bottle.

the methylated spirit dissolves and the bromoform can be drawn off and suitably dried. This method is followed in principle in the author's laboratories, employing 99% industrial methylated spirit.

¹ *Geol. Mag.*, 70, 1933, p. 192.

About 200 ml. of bromoform-alcohol washings are placed in a 2,000 ml. separating cylinder and about 1,500 ml. of water added and the mixture shaken. The bromoform separates to the bottom of the funnel where it may be run off and dried for re-use, unless, as sometimes happens in separation of residues from bituminous rocks, it appears very dark in colour, in which case it is advisable to redistil. Bromoform is not so readily soluble in alcohol as in benzol and for this reason washing requires to be carried out with care. An effective way of rapidly removing the bromoform is to direct a fine jet of alcohol on to the filter paper, using a wash bottle fitted with a rubber blow-ball.

In order to economize in the use of 'heavy' liquid, take the smallest amount of cleaned sample which is practicable. This implies from 10–15 g. in the case of average silts (0.05 mm.–0.1 mm. grade); 15–20 g. of fine to medium sand (0.1 mm.–0.5 mm.); 25 g. of coarse sand (> 0.5 mm.); coarse sands and gravels should be panned (the latter screened) to reduce bulk of material; the same applies to clays; see, however, p. 124.

A form of apparatus commonly employed for heavy mineral separations is shown in the accompanying diagram (Fig. 5) and is self-explanatory. The bottles used to hold bromoform and bromoform 'washings' should be plainly labelled or 'washings' may be accidentally added to the bottle containing pure bromoform. The sample is poured into the upper funnel and constantly stirred, at least half an hour being necessary to ensure a good separation. It is doubtful whether a 100% separation can ever be effected in practice, but with care it should be reasonably complete. Filtering may in some cases be accelerated by using fanfolded- filter papers, obtainable from most makers. Both the light and heavy residues are washed free of bromoform with benzol and subsequently dried in a steam-oven or over a sand-bath. Other forms of separating apparatus, *e.g.* Spaeth, may commend themselves to the reader (Fig. 7, p. 121).

When dry, the residue may be further subjected to special treatment for specific mineral concentration, including magnetic separation and the employment of other 'heavy' liquids or fused salts: see p. 119.

HEAVY RESIDUE SAMPLING

It frequently happens that a heavy mineral residue obtained by bromoform or other separation is too large to be mounted on a single microscope slide. The problem of sampling has then to be faced. As G. H. Otto¹ points out, errors of sampling may be incurred

¹ Comparative Tests of Several Methods of Sampling Heavy Mineral Concentrates, *Journ. Sed. Pet.*, 3, 1933, p. 30.

through inability to produce the true conditions of random sampling or alternatively to factors which shift the 'observed modal frequency of a component from its true value'. Owing to difference in size, shape, density, magnetic properties, coefficient of friction and elastic properties of grains, it is most unlikely that a truly representative sample can be obtained by means of a spatula.

Probably the simplest procedure in most cases is to place the heavy mineral residue on a sheet of glass and quarter it with a strip of stiff paper, continuing the process until a portion of the desired weight is obtained.

Attempts have been made to apply mechanical methods of sampling relatively large masses to these residues, but usually without much success. W. C. Krumbein designed a conical hopper with a very small opening at the tip; this opening is placed over the intersection of two knife-edges placed at right angles to each other. The sample when poured through the hopper is thus split into four portions, two of which are rejected and the other two passed through the hopper again and the process repeated until a suitably sized sample is obtained.

Where a sample of 25 g. or more is required from a large quantity of material, the Jones ore-sample splitter is frequently employed. This is fitted with a long narrow hopper into which the material is poured and divided equally into two pans by means of a series of inclined chutes. The material in one pan is passed through the hopper again and the process repeated until a sample of requisite size is procured.

This apparatus, however, is not suitable for very small samples, the chutes being constructed of folded sheets of iron. G. H. Otto designed a machine known as the 'Microsplit' which is based on the same principle as the ore-sampling splitter, but which has for the inclined chutes a series of 16 brass plates each $\frac{1}{16}$ in. thick with polished inclined edges. Thin bronze partitions separate the plates and the parts are held together by screws after pressure in a strong vice. It is claimed for this device that it is far better than using a spatula or pouring a few grains from a vial and results certainly seem to support this contention. Moreover, it is very quick in operation.

C. K. Wentworth, W. L. Wilgins and H. L. Koch¹ later described two rotary sample splitters, one for large samples of coarse material and the other for small samples of heavy minerals, but each of similar design.

The mega-splitter embodies a plywood turntable mounted on a vertical steel axle the hardened points of which pivot in adjustable centre screws. In a circle concentric with the axle are mounted

¹ A Rotary Type of Sample Splitter, *Journ. Sed. Pet.*, 4, 1934, p. 127.

sixteen 4 oz. metal pill-boxes and a funnel is arranged directly over this circle so that on rotation the boxes pass in turn under the funnel. The axle is spun by hand and the rate of turning can thus be adjusted as required. The sixteen original samples may be used, or, by combining opposite sixteenths, eighths can be formed; similarly quarters by taking each fourth sixteenth or halves by taking alternate sixteenths, may be formed. By halving in this way and successive repetition of the procedure, the desired fraction can be obtained.

The micro-splitter is similar in design but is fitted with 16 small glass vials in place of the metal pill-boxes. Difficulty is experienced with very small samples in producing a slow, steady stream of mineral grains, but is overcome by mounting a small piece of glass tubing on a pair of trundle rollers driven by a rubber band belt from a small hand-crank. The turntable is rotated from the same crank by another belt. A small funnel with an elongated outlet is used to reduce loss of grains by bouncing on the edges of the moving vials. Tests of these machines show that more accurate results are thus obtained than with other known sample splitters.

MOUNTING OF SAND GRAINS FOR MICROSCOPICAL EXAMINATION

The final operation consists in mounting the residue or concentrated material with Canada balsam on a glass slip and is similar in many respects to the technique described for thin sections (p. 85), except that it is a little more difficult to attain complete expulsion of air-bubbles. It is advisable wherever possible to mount the total residue for microscopical examination; by so doing, risk of losing rare species is minimized. The different magnetic crops, if isolated (p. 198), are mounted separately and a representative sample of the light material may also be mounted. Glass microscope slips (3 in. \times 1 in.) and thin cover-glasses ($1\frac{1}{4}$ in. \times $\frac{7}{8}$ in. or $\frac{3}{4}$ in. square) are the most useful sizes. Non-permanent mounts may be made by using ordinary cedar oil, R.I. 1.516; or air-mounts, especially of micro-organisms, may be preferred.

The exclusion of air-bubbles has been mentioned. This process is aided by moistening the cover-glass with turpentine or xylol before pressing it down on to the slip; this may be varied by putting the grains on to the moistened cover-glass and then pressing it down on to the slip on which the balsam is sufficiently heated. A little careful 'to-and-fro' motion imparted to the cover-glass with tweezers, while the balsam is still hot, is often all that is necessary to obviate the presence of such bubbles.

Solution of surplus balsam is rapidly obtained as before (p. 87) by using methylated spirit or benzol, a final immersion of the slide

in ether being advantageous, but not necessary. Xylol is probably the quickest solvent, but it has an unfortunate habit of eating into the balsam under the cover-glass and thus impairing the mount.

With minerals or rock-fragments capable of passing through a 36-mesh B.S. sieve, little difficulty, save with air-bubbles, is experienced in mounting with Canada balsam, but with larger material (> 36), unless an inordinate thickness of balsam is used, the method is not practicable. Some workers employ satisfactorily vulcanite rings cemented either by a special gum or with balsam to the slide; more balsam is then put into the ring, together with the material to be mounted and when cooked, a circular cover-glass is affixed; this is an old method, but one which with care is reasonably satisfactory, though uncooked or too highly coloured balsam, or air-bubbles, may be troublesome. Another method is to employ microscope slips in which a shallow, bowl-shaped hollow has been ground on one surface; such slips are very useful for air-mounts of *foraminifera*.

A. W. Slocum and E. T. Thomas¹ devised a neat form of mount which is very useful for micro-organisms and large mineral grains. It consists of a celluloid strip 24 mm. \times 60 mm. (of thickness to suit the material) punched at regular intervals by means of an ordinary paper punch giving about 4 mm. holes. The celluloid strip is then cemented to an ordinary glass slip with acetone. Each 'cup' thus prepared will receive a grain or organism, which may be cemented in any particular position (if desired), or may be left free as an air-mount. A thin cover-glass, of same length and breadth as the strip, is then cemented on to it with acetone, thus completing the mount. The value of this mount lies in the possibility of preserving on one slide characteristic mineral grains of a peculiar assemblage or representative micro-organisms from a particular horizon, etc.

Where a black background is preferred, as is often the case with coloured minerals or *foraminifera*, a similar slide can be made of cardboard suitably punched and glued on to a piece of thin black cardboard of identical size, as described by G. D. Hanna and H. L. Driver². From the point of view of permanence, however, the celluloid-glass combination has much to recommend it.

A. C. Tester³ utilizes a novel method of mounting *foraminifera*, other small organisms or heavy mineral grains. Ordinary cardboard slides with a cut-out are employed with a thin cover glass at the bottom of the cut-out to produce a stronger light effect on the under side of the mineral grains. A strip of cellophane is then fixed with

¹ Bull. Amer. Assoc. Petrol. Geol., 9, 1925, p. 667.

² The Study of Subsurface Formations in California Oilfield Development, 10th Ann. Rep. Calif. State Min. Bur., 10, 1924, No. 3, p. 5.

³ Journ. Sed. Pet., 2, 1932, p. 125.

cement or glue to the top of the slide. To effect the cellophane covering, a thin strip about $\frac{1}{4}$ in. wider than the opening of the slide is cut and the ends twined over and cemented on the under side of the slide. A smooth and dust-proof cover results if sufficient care is taken to pull the cellophane strip taut. The advantages of cellophane over a thin cover glass are numerous. The slide does not break if dropped, it can be pressed in handling and generally submitted to rougher treatment. Further, cellophane is about $\frac{1}{4}$ th the thickness of an average cover glass, which is advantageous when high-power objectives are employed; if the objective touches the slide, the cover slip of cellophane yields slightly but does not break; neither does it scratch the objective as a glass slip is liable to under pressure.

SYSTEMATIC PROCEDURE FOR SIMULTANEOUS INVESTIGATION OF SAMPLES FOR MICRO-ORGANISMS AND HEAVY MINERALS

The extended use of petrological and micropalaeontological methods of subsurface correlation in the principal oilfields of the world has compelled development of a special technique for handling simultaneously several samples rather than single specimens, as has been customary in the past. This technique, while differing in detail according to local circumstances and demands, is, in its broader outlines, applicable to all large-scale operations of this description, whether of academic or economic purpose. With increased facilities for obtaining rock-samples under practically all conditions of exploratory work, improved methods of preparation and analysis have evolved collaterally, so that the fullest possible stratigraphical evidence may be elucidated from a series of samples with minimum time and preliminary treatment.

Apart from special manipulation of samples for their heavy minerals as a basis of petrographic methods of correlation, the work of palaeontologists on the micro-organic contents of such samples (including *foraminifera*, *diatomacea*, *bryozoa*, *radiolaria* etc.) as standardized by the geological staffs of oil companies operating in United States, Middle East and elsewhere, has had a marked effect on the trend of organization of laboratory work for the exhaustive investigation of well-samples. The most detailed, hence the most valuable, *subsurface* stratigraphical evidence to be obtained from any kind of sedimentary rock is that which is compounded of palaeontology and petrology; correlation based on one or the other may be entirely satisfactory as a practical expedient and limited to local conditions; correlation based on the cumulative evidence of both lines of investigation carries with it the support of strong scientific probability and is accordingly more exact and certainly of greater consequence.

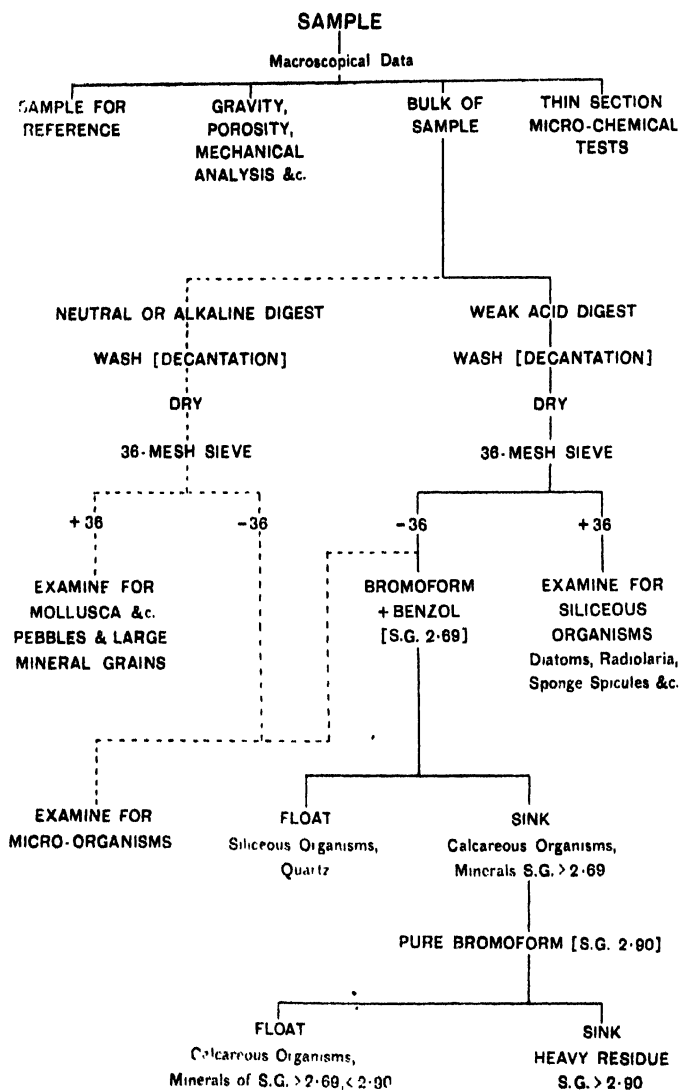
Such comprehensive analysis of sedimentary rocks represents the ideal to which all relevant research should tend, though for obvious reasons its attainment is largely restricted to those spheres of oilfield activity where highly trained technical staffs enjoy full laboratory facilities for the prosecution of such work.

Pursuing each line of investigation exclusively implies independent treatment of separate portions of a sample for its heavy minerals and its micro-fossils, a duplication of preparatory work which is an unnecessary waste of time. The development of a systematic procedure for simultaneous extraction of both constituents became, therefore, a desideratum, especially in large-scale work and a few attempts to formulate such a plan were made by American workers with varying degrees of success, in particular that devised by G. D. Hanna and H. L. Driver¹.

Experience with all kinds of rocks, surface samples, oil-well samples, cores, 'cuttings' and the like, has resulted in the adoption by the author of the procedure detailed in the following paragraphs. This plan of operation has the advantage that, although it makes for routine practice which can be carried out by non-technical assistants under supervision, it is sufficiently elastic at critical stages to be adaptable to special circumstances which may arise during the course of investigations. The ultimate success of this procedure depends to some extent, however, on the initial measures adopted for classifying the samples, not only as a basis of their comprehensive analysis, but also for purposes of collateral and future reference; accordingly some system, such as that already described for filing information (p. 71), is an essential preliminary to this technique.

Before proceeding with treatment of the samples, the batch should be arranged in definite order; they should not be selected indiscriminately. With samples derived from the same oil-well, the series should be made up in ascending or descending order according to depth, the deepest being taken first and working gradually upwards to those nearer the surface, or *vice versa*; where investigations are proceeding collaterally with drilling the well, as is often the case, obviously the reverse order will be maintained, each batch of samples being dealt with in order of depth as they are received from the well. With outcrop samples some similar system should be adopted, implying a geographical sequence, *e.g.* direction of traverse, strike direction, vertical sequence (quarry-face, cliff-section, etc.), stratigraphical sequence, and so on. The advantage of such orderly procedure will readily be appreciated when the treatment of a series of related samples is contemplated, since connected results automatically emerge as the work progresses.

¹ *op. cit.*



The 'flow-sheet' (p. 110) shows in concise form the plan of procedure. Where only heavy mineral concentrates are sought, standard methods of separation previously described hold good, though modifications in apparatus for dealing with a number of samples at the same time are noted below (p. 114). Where organisms only are required and where it is desired to segregate calcareous and siliceous forms, the procedure need only be followed as far as the bromoform-benzol stage, though final treatment with bromoform to get rid of heavy minerals, especially if much pyrite occurs (p. 123), is often advantageous. Samples which are impregnated with petroleum residues require special treatment at the outset (p. 117).

Macroscopical Data. (See also p. 81). In the first instance the sample is spread out on white paper or in a large shallow evaporating basin for macroscopical examination, aided by hand-lens. A record is then made of the colour, lithological nature, pebble constituents and shell-fragments (if any), etc., which may be apparent. Approximately three-quarters of the sample is then taken to constitute the 'bulk-sample'; the remaining quarter is divided into a portion for reference ('key-sample'); a portion for physical tests if desired (*e.g.* specific gravity, porosity, mechanical analysis) and, if required and practicable, a suitable piece is selected for thin section preparation which, apart from the microscopical examination in the usual way, can subsequently be utilised for any particular microchemical tests; in the case of physical tests, where these are of paramount importance, probably more than the suggested amount (25%) of the original sample will be utilized: it depends largely on the quantity of the sample initially available¹.

With core-samples and compact rocks such as shales, mudstones, etc., it is necessary to break these down before proceeding, bearing in mind, in the case of core-samples, the precautions already noted (p. 64). Such disintegration can generally be accomplished by splitting the material parallel to any prevalent lamination or bedding and then crumbling the laminae or fragments thus obtained with the fingers or with the aid of a pestle and mortar; drastic pulverization is to be avoided wherever possible. In refractory cases, several methods have been devised to promote disintegration; heating the sample and then plunging into cold water is one common method; other methods consist in boiling the fragments with caustic soda; in covering the crushed sample with an equal amount of sodium acetate, adding a few drops of water and heating, when the crystals melt; the sample becomes saturated with the solution and on cooling the addition of a crystal of the acetate causes crystallization, the force thus exerted determining the disintegration of the rock particles²; a similar result can be achieved by the use of sodium thiosulphate³. An application of

¹ For relevant methods and calculations, A. Holmes' *Petrographic Methods* (Murby, London), 1921, Chapters 2 and 5, should be consulted.

² M. Guinard, *Journ. Queckett Micros. Club*, 1888, Ser. 2, iii, p. 188.

³ G. D. Hanna and H. L. Driver, *op. cit.*, p. 14.

A. Mann's method¹ of disintegrating diatomaceous shales also suggests itself: this consists in boiling the fragments for a few moments with sodium carbonate solution and then quenching with hydrochloric acid; the evolution of carbon dioxide has the effect of breaking down the shale successfully.

Disaggregation (as it is called) of partly or wholly consolidated sedimentary rocks depends largely on grain-size of particles or crystals and on nature of cementing medium. It has received considerable attention by many workers in this field². To the methods above suggested may be usefully added:

- (a) soak in water and freeze ('dry ice'—solid CO_2 —is effective here);
- (b) boil in concentrated solution of ammonium nitrate and cool rapidly;
- (c) with ferruginous cements, boil with 15–20% hydrochloric acid + 10% stannous chloride;
- (d) with silica cement, boiling with concentrated sodium or potassium hydroxide is sometimes effective;
- (e) with argillaceous rocks *e.g.* shale, mudstone, if dispersion is difficult by ordinary means, crush into small fragments, place in N/100 solution of sodium oxalate and agitate³.

'Bulk-Sample'. The 'bulk-sample' is divided into two portions, one digested with weak hydrochloric acid (1 : 4 or weaker): 'acid digest'; the other is treated with caustic soda: 'alkaline digest'. If known to be rich in calcareous organisms, treat the major part of the sample with alkali. In both cases gentle though possibly prolonged heating accomplishes clarification and in the case of the acid, removal of soluble minerals and calcareous organisms, which, however, are preserved in the alkaline digest.

Acid Digest. The authigenic material, mud or scum resulting from this digestion is washed away with cold water by decantation, the remaining portion being dried over a sand-bath or in a steam-oven. When dry and cold, it is passed through a 36-mesh sieve; the >36 material is examined carefully for the larger siliceous organisms (diatoms, *radiolaria*, sponge spicules, etc.), significant rock-fragments, pebbles or mineral grains; large constituents are picked out by hand or with tweezers, the smaller organisms etc., with a camel-hair brush moistened with glycerine or cedarwood oil, usually under a strong hand-lens. All or a portion of the <36 material, depending on the quantity, is next transferred to the bromoform-benzol solution of sp.gr. 2.68–2.70. This solution serves to float off the smaller siliceous organisms and the light minerals (including quartz) of sp.gr. < 2.68–2.70. The material which sinks is the heavy mineral residue plus any

¹ A. Mann, *Proc. U.S. National Mus.*, **60**, 1922, p. 1.

² W. C. Krumbein and F. J. Pettijohn, *Manual of Sedimentary Petrography*, (D. Appleton-Century, New York), 1938.

³ E. E. Wahlstrom, *Petrographic Mineralogy*, (Wiley, New York), 1955, p. 3. See also W. H. Twenhofel and S. A. Tyler, *Methods of Study of Sediments* (McGraw Hill, New, York), 1941, pp. 39–45.

calcareous organisms which may have escaped destruction by the acid treatment. The light and heavy fractions are dried.

Alkaline Digest. The alkaline treatment serves to clarify the other portion of the 'bulk-sample' and aid detection of calcareous organisms; incidentally, it helps in disintegrating the particles if there has previously been some difficulty in doing this. The scum is again washed off by decantation, taking care not to lose anything but the muddy matter, and the residue dried over a sand-bath as before. It is then passed through a 36-mesh sieve; the > 36 material is segregated and examined for the more prominent pebble constituents, large mineral grains, molluscan or other fossil organisms which may be separated by hand, as with the similar product from the acid digest. The < 36 material is next added to the < 36 material from the acid digest and the whole passed into the bromoform-benzol solution; or, if preferred for any particular reason, the bromoform-benzol concentration may be carried out separately on both lots. As explained above, this solution has the effect of floating off the light minerals (quartz) and the siliceous organisms which can thus easily be concentrated; calcareous organisms, preserved by the alkaline digest, are left behind with the normal heavy mineral suite. Some difficulty may be experienced at this stage in getting the calcareous organisms to sink completely if, in the case of *foraminifera*, the previous treatment has resulted in the cells filling up with air; this can be overcome to a large extent by very complete stirring and by constantly depressing the material with a glass rod well into the solution.

Bromoform Separation. The last stage in the process consists of floating off with bromoform (sp.gr. 2.9), the calcareous organisms (*foraminifera* particularly) and minerals of sp.gr. > 2.68 – 2.70 and < 2.9 from the ultimate heavy mineral residue (> 2.9) used in petrographic methods of correlation. Thus a microscope slide of the 'light' material will consist principally of a concentrate of calcareous organisms minus quartz, the desired end in view, since it saves the necessity of tedious hand-picking of minute bodies under the microscope.

Simultaneous separation of at least two dozen concentrates (either with the bromoform-benzol solution or with bromoform alone) is achieved by use of a funnel-battery capable of holding 24 funnels with corresponding drainers as shown in Fig. 6. Two of these batteries side by side are employed, one for bromoform-benzol separations, the other for normal bromoform separations, concentrates being passed on from the first to the second automatically. Those accustomed to carrying out single bromoform separations will readily appreciate the great saving of time and labour afforded by such large-scale operations. It may be argued that bromoform is expensive to use in this way, but 2 lb. of the liquid will be ample to fill 24 funnels with an adequate amount, and ultimate loss through volatilization is not much greater, if care be taken, than when using the same amount for successive single separations; also, use of bromoform on this scale adds considerably to the quantity of bromoform washings (in benzol) at any one time, so that it pays to redistil the washings for recovery of heavy liquid at

the end of a day's run. The supervision of two of these funnel-batteries in simultaneous operation renders it possible to dispose of well over one hundred samples in a comparatively short time.

At first glance the foregoing procedure may seem somewhat complicated, but a trial will prove its efficacy and comparative simplicity of operation. It is not contended that the plan is an infallible one or that cases do not arise where certain departures from the routine may be desirable, but where separate concentrations of groups of organisms and heavy minerals are required from a number of samples with some degree of rapidity, the procedure has everything to commend it. Its success is more readily assured by having

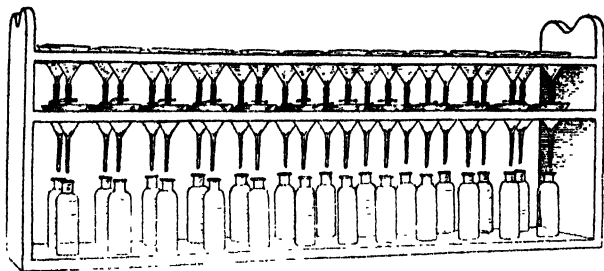


FIG. 6. Funnel-battery for Bromoform Separation.

the requisite apparatus always handy, keeping special dishes, sieves, etc., apart for the two different digests; apparatus used for alkaline treatment may conveniently be designated with a blue mark on each article, that for acid digest, with a red mark; in this way confusion of products is avoided during operations.

The acid and alkaline solutions should be made up ready in Winchester quart bottles and suitably labelled; sufficient bromoform-benzol solution should be made up for one batch of samples at a time and not in too great a bulk, since it is liable to deteriorate on keeping, as already mentioned (p. 102). The real secret of successful work on these lines lies in the establishment of the necessary organization, including equipment, under which the several operations can be carried on uninterruptedly; shortage of apparatus, intermittent attention, incorrect solutions (as regards gravity), or, what is worse, inability to 'keep one's head', are one and all certain causes of failure.

SPECIAL METHODS OF CONCENTRATION: PANNING

Where the initial bulk of a sample is greater than that desired for heavy mineral analysis, it may be conveniently reduced by the ordinary process of panning under running water in a wide, open

tray, developing dish or evaporating basin. The secret of success here lies in the ability to give a combined circular and 'to-and-fro' motion to the water; this has the effect of swirling out the lighter and finer constituents, which are carefully poured off and concentrating the larger and heavier grains. Skilful panning should not result in any appreciable loss of heavy mineral.

Exactly the same process is carried out when operating on fine-grained rocks, *e.g.* clays, shales, etc., and crushed rocks (p. 127). It has also been used with some degree of success in cases where heavy liquids have not been available for mineral concentration.

In the matter of panning as preliminary to heavy mineral concentration, certain warning is necessary to those without experience of this procedure. C. J. Ewing¹ pointed out that the two most common methods of heavy mineral separation adopted (bromoform separation and panning in water) imply apparatus and technique which are by no means standard; further, many investigators carry out preliminary panning of the material prior to separation by bromoform. Vastly different results, he maintained, are achieved with material which has been subjected to preliminary panning and material which has been subjected to bromoform separation alone and he gives convincing data in support of this claim.

His procedure briefly was to take in each case four 10 g. samples, of which first and third were subjected to panning and second and fourth to direct bromoform separation. A 'steep sided' 9 in. evaporating dish was used for panning with no inward groove at the edge. Usually only one panning was deemed necessary, but in some cases samples were panned three times as a check. The residue from panning in each case lay between 5% and 10% by weight of the original sample. After drying, this residue was passed through bromoform. The whole of the residue was then mounted. To expedite the work of counting, a system of keys, each one operating a 'Veeder' counter was employed.

Omitting opaque minerals, the species counted were zircon, rutile, staurolite, kyanite and tourmaline, but actually results were only considered representative for zircon, staurolite and tourmaline. Comparison of ratios between panned and non-panned materials showed a consistent excess of zircon in panned results, close similarity in the figures for staurolite and a consistent loss in panning in the case of tourmaline.

Retention of heavy grains in the 'light' crop was probably attributed to 'size of grains, density, surface tension and the time factor'. Zircon, which has an average diameter of 0.1 mm., thus fills the interstices between the larger quartz grains and impedes sinking. Tourmaline, having only a slightly greater density than bromoform and also being found in 'flat faced' grains, causes partial exclusion from the heavy fraction.

¹ A Comparison of the Methods of Heavy Mineral Separation, *Geol. Mag.*, 68, 1931, p. 136.

If an indefinite time were taken over the separation and constant stirring employed, each grain would obviously ultimately make its way to the clear bromoform. For an ideal separation the quartz layer should only be one grain thick when practically no obstruction could occur. The personal factor also enters largely into the problem of panning, as frequently grains are lost during the process.

Probably the best way of achieving a uniform method of separation is by a compromise between panning and bromoform separation. The loss of minerals would not be great if panning were used to reduce the bulk to one-half, as it is in the final stages that the greatest loss occurs. The samples after drying could be passed through bromoform in the usual way and the absence of much quartz at this stage would prevent obstruction of grains in their way to the clear bromoform.

CENTRIFUGAL METHODS

Workers on sediments are all familiar with the difficulties of extracting reasonable heavy residues from the finest grades such as clays, suspensions in asphalt, limestones, etc. In fact, in some cases ordinary bromoform or other heavy liquid method, owing to surface tension or other effect, is quite inadmissible. The first apparently to apply centrifugal methods was F. von Wolff¹, who used acetylene tetrabromide or Clerici's solution (p. 120) in a special form of sling-tube; by suitably heating the centrifuge he was able to employ successfully fused salt diluted with silver nitrate for minerals of higher sp.gr. than 4.2. I. C. Brown² developed a special quantitative method of separating heavy minerals with bromoform, by suitably modifying the normal type of centrifuge tube in fixing to it a small cylindrical glass container to catch the minerals when thrown down. F. Schroeder³ and W. Kunitz⁴ have worked on similar lines with specially shaped sling-tubes.

The method for some time past employed in the author's laboratories was developed particularly to deal with heavy minerals from (1) fine sediment in native asphalts or bituminous rocks irrecoverable by any other means; (2) rock powders (e.g. limestone) containing a very small amount of heavy residue, and (3) sediment of a type where grain-size is small and therefore rate of sedimentation of

¹ Die Trennung fester Phasen durch die Zentrifuge, *Centr. f. Min., A*, 1927, p. 449.

² A Method for the Separation of Heavy Minerals of Fine Soil, *Journ. Paleont.*, 3, 1929, p. 412.

³ Scheidetrichter zum Einsetzen in die Zentrifuge beim Trennen von Mineralgemischen mit schweren Flüssigkeiten, *Centr. f. Min., A*, 1930, p. 38.

⁴ Eine Schnellmethode der gravimetrischen Phasenanalyse mittels der Zentrifuge, *Centr. f. Min., A*, 1931, p. 225.

particles in bromoform low. As this technique is quite simple to employ, does not call for expensive equipment, and is equally applicable to all sediments or crushed rocks, particularly for heavy mineral extraction, a full account is given here.

With bituminous impregnated rocks special initial preparation must be undertaken to obtain satisfactory heavy residues. In the first place the impregnating bitumen must be extracted as completely as possible before any attempt is made to recover heavy minerals. The best way of effecting this is to take at least a 100 g. sample and employ the method described on p. 261 for determination of soluble bitumen. After drying the residual mineral matter in an oven, it is removed from the filter paper and treated with cold 6N hydrochloric acid until effervescence ceases. Care is taken to avoid undue excess of acid. The liquid is then filtered through a Buchner funnel, the residue being washed with water and dried in an oven.

One to five g. of the insoluble matter are placed in a centrifuge tube about 4 in. long and $\frac{3}{4}$ in. in diameter and 10 ml. of bromoform added, the mixture being stirred to ensure that the powder is completely wetted. The tube is then placed in a centrifuge and whirled for half to one minute. A small hand-driven machine capable of about 1,500 r.p.m. is quite satisfactory for this purpose if a higher-speed machine is not available.

The light residue forms a cake on the surface of the bromoform and can be removed almost completely with a spatula without disturbing the remainder of the solution. The tube is then rapidly inverted over a beaker and held in an inverted vertical position whilst any light residue adhering to the sides of the tube is wiped away with the finger. The heavy residue adheres to the bottom of the tube and can later be washed out with methylated spirit. It is essential to keep the centrifuge tube in an inverted position whilst removing the last traces of light residue, otherwise the latter may run down and contaminate the heavy residue.

When the sides of the tube are clean, the heavy residue is washed out with methylated spirit on to a watch glass and the excess of liquid poured off. In some cases, the residue may now be clean enough to mount, but usually the grains are contaminated with carbonaceous matter which interferes with subsequent identification of the minerals. One of the most satisfactory methods of cleaning the residue is to treat it with 1 or 2 ml. of 100 vol. hydrogen peroxide and warm on the steam-bath until oxygen begins to be evolved. The watch glass is then removed and the liquid stirred until the reaction ceases, when dilute hydrochloric acid is added and the mixture allowed to stand for a short while. The excess of acid is poured off and the residue carefully washed, first with water and then with alcohol and dried, when it is ready for mounting. This treatment naturally removes a considerable amount of pyrite (if present) and cannot be adopted in all cases. Alternative cleaning agents are chloric acid or dilute nitric acid to which a few drops of alcohol are added.

For preparation of heavy residues from the acid-washed material

removed from a mastic asphalt, a 2 g. sample is ample and it is usually a definite disadvantage to take more. If a greater quantity of heavy residue is required, it is better to centrifuge in two separate portions. For sands and other coarse rock powders, it may be necessary to take up to 5 g.

C. B. Claypool and W. V. Howard¹ have used a special technique, involving heavy liquid separation with a centrifuge, applicable to *calcareous* oil-well cuttings, essentially to determine the relative quantities of calcite and dolomite in such samples. The heavy liquid employed is mercuric potassium iodide (Thoulet's solution). Their procedure is as follows:

2 ml. of the sample ground to pass an 80-mesh sieve are placed in a 15 ml. graduated centrifuge tube. Approximately 10 ml. of the heavy liquid diluted to a sp.gr. 2.75 are added and the whole mixed thoroughly by means of a glass rod and shaking. The mixture is then centrifuged for 3 to 5 minutes at about 700r.p.m. The light fraction, or floating material, is then poured off into another tube. If separation is incomplete, the operation may have to be performed twice. The light fraction is then re-centrifuged to remove any heavy material which may be present, decanted and sufficient water added to sink it all. It is again centrifuged and all the liquid poured off. A volume determination of the light fraction is then made. Hydrochloric acid is slowly added to the measured fraction until effervescence ceases. The insoluble residue is centrifuged for about 3 minutes and the volume of sand and shale fractions determined directly. The volume of calcite is calculated by difference.

The medium fractions are then all collected together and centrifuged in the undiluted heavy liquid (sp.gr. 3.05). The solution and that portion of the sample which floats is subsequently poured off, leaving the heavy fraction as residue. Water is added as in the case of the light fraction and the liquid decanted after centrifuging. The volume of the medium fraction having been determined, concentrated hydrochloric acid with a little nitric acid is added until effervescence ceases when heated on a water bath. The residue is then centrifuged and the volume of dolomite calculated by difference.

The heavy fraction obtained during the above procedure is mixed with water to dissolve any iodides which may have crystallized out. Its volume is then measured and the same procedure with hydrochloric and nitric acids followed as for the medium fraction. Magnesite can then be calculated by difference.

Results obtained with this technique show a high order of accuracy as compared with those obtained by examination of large fragments stained with Lemberg's solution. In each case, however, the insoluble fraction recorded is larger than that calculated from analyses. This is due to the fact that during the course of analysis finer grinding is employed and complete separation of insoluble from soluble material achieved by frequent evaporation to dryness. It would not, however, be practicable to grind the material finer than to 80 mesh for the

¹ Method of Examining Well-Cuttings, *Bull. Amer. Assoc. Petrol. Geol.*, 12, 1928, p. 1147.

centrifuge method owing to the difficulty of sinking very fine grains in water. The margin of error is never, in any case, of detriment to final results.

HEAVY LIQUIDS AND SUBSTANCES OTHER THAN BROMOFORM FOR MINERAL SEPARATION

If it is desired to segregate a particular mineral or suite of minerals from (generally) an initial bromoform residue, apart from methods detailed in Chapter V, use may be made of different liquids and/or fused salts or mixtures. The following is a list of some of the more important media which have been described and used^{1, 2, 3, 4, 5, 6, 7}:

Acetylene tetrabromide.	Sp.gr. 1.6–2.95. Dil. chloroform or benzene.
Antimony tribromide.	Sp.gr. 3.11–3.65. M.P. 94.2°C. Dil. water.
Antimony trichloride.	Sp.gr. 2.59 at 100°C, 3.06 at 26°C. Dil. Water.
Arsenic tri-iodide <i>plus</i> antimony iodide in solution of arsenic tribromide and methylene iodide.	Sp.gr. 3.70 at 20°C.
Barium bromomercurate.	Sp.gr. 3.11 at 11°C., 3.14 at 18°C.
Barium mercuric nitrate.	Sp.gr. 3.59. (Rohrbach's solution).
Cadmium borotungstate.	Sp.gr. 3.36. Dil. water. Remove carbonates before separation with this compound.

¹ E. Clerici, Preparazione di liquidi per la separazione dei minerali, *Rend. R. Acad. Lincei*, ser. 5, 16, 1907, p. 187.

² J. W. Retgers, Ueber schwere Flussigkeiten zur Trennung von Mineralien, *N.J.f. Min.*, ii, 1889, p. 185.

Die Bestimmung des specifischen Gewichte von in Wasser löslicher Salzen, III. Die Darstellung neuer schwerer Flussigkeiten, *Zeitschr. f. physik. Chemie*, 11, 1893, p. 328.

Thalliumsilbernitrat als schwere Schmelze zu Mineraltrennungen, *N.J.f. Min.*, i, 1893, p. 90.

Versuche zur Darstellung neuer Schwerer Flussigkeiten zur Mineraltrennung, I. Die Acetate der Schwermetalle als schwere Schmelzen, *N.J.f. Min.*, i, 1896, p. 212.

Versuche zur Darstellung neuer Schwerer Flussigkeiten zur Mineraltrennung, II. Die Nitrate und Doppelnitrate der Schwermetalle als schwere Schmelzen, *N.J.f. Min.*, ii, 1896, p. 183.

³ C. Rohrbach, Ueber die Verwendbarkeit einer Baryumquecksilberjodidlösung an petrographischen Zwecken, *N.J.f. Min.*, ii, 1883, p. 186.

⁴ E. Sonstadt, Note on a new method of taking specific gravities, adapted for special cases, *Chem. News*, 29, 1874, p. 127.

⁵ J. D. Sullivan, Heavy Liquids for Mineralogical Analyses, *U.S. Bur. Mines Tech. Paper* 381, 1927.

⁶ J. Thoulet, Note sur un nouveau procédé d'étude au microscope des minefaux en grains très-fins, *Bull. Soc. Min. France*, ii, 1879, p. 188.

⁷ H. E. Vassar, Clerici solution for mineral separation by gravity, *Amer. Min.*, 10, 1925, p. 123.

Carbon tetrachloride.	Sp.gr. 1.58-1.61.
Lead chloride.	Sp.gr. 5.0.
Lead tetrabromide.	Sp.gr. 3.5.
Lead tetrachloride.	Sp.gr. 3.18 (0°C.). M.P. - 15°C. Decomposes violently at 105°C, avoid heating.
Lead-zinc chloride.	Melt together in all proportions to give compounds of varying sp.gr.
Mercuric nitrate.	Sp.gr. 3.3-3.4.
Mercuric potassium iodide.	Sp.gr. 3.18. Keep mercury in bottle. Attacks rubber.
Mercurous nitrate.	Sp.gr. 4.3. M.P. 70°C. Dil. water.
Methylene iodide.	Sp.gr. 3.32 at 16°C.
Methylene iodide <i>plus</i> iodine.	Sp.gr. 3.548.
Methylene iodide <i>plus</i> iodoform.	Sp.gr. 3.60-3.65.
Selenium mono-bromide.	Sp.gr. 3.6 at 15°C. Decomposed by heat; reacts with water.
Sodium mercury iodide.	Sp.gr. 3.46.
Stannic bromide.	Sp.gr. 3.35 at 35°C. M.P. 30°C.
Stannic chloride.	Sp.gr. 2.279 at 0°C., 2.27 at 20°C. M.P. - 33°C. Dil. water.
Stannic iodide.	Sp.gr. 4.70 at 15°C. M.P. 143°C.
Stannic iodide <i>plus</i> arsenic tri- bromide.	Sp.gr. 3.73.
Tetrabromethane.	Sp.gr. 2.9.
Thallous acetate and nitrate.	Sp.gr. 4.5.
Thallous formate.	Sp.gr. 3.31 at 10°C., 3.40 at 20°C., 4.10 at 50°C.
Thallous formate <i>plus</i> fluoride.	Sp.gr. 4.20 at 20°C., 5.38 at 100°C., 5.40 at 110°C.
Thallous malonate <i>plus</i> formate.	Sp.gr. 4.0 at 10°C., 4.7 at 50°C. (Clerici solution).
Thallous mercurous nitrate.	Sp.gr. 5.3. M.P. 76°C.
Thallous <i>plus</i> silver nitrate.	Sp.gr. 4.6. M.P. 75°C. Attacks sulphides.
Zinc chloride.	Sp.gr. 2.4. Zinc chloride and lead chloride melt together in all proportions to form mixtures of varying sp.gr.

Mixtures of any two of the following have been successfully employed in special cases:

Lead Nitrate.
Mercuric Nitrate.
Silver Nitrate.
Thallous Nitrate.

The above media for heavy mineral separation can conveniently be divided into (1) those which are used as liquids at ordinary

temperatures and (2) those which have to be fused or melted before use. In a large number of cases, the compounds are exceedingly poisonous and the greatest care should be taken in their manipulation.

In the case of most of the liquids, since they are expensive, economy is required in their use. Much smaller funnels should be used than with ordinary bromoform separation. Alternatively a small separating funnel fitted with secure stopcock may be employed; or the simple apparatus described by F. J.

Fraser¹, consisting of a tube wider at one end than the other and bent into a 'U' shape. The tube is two-thirds filled with bromoform or other liquid employed and the concentrate introduced into the wider limb. This limb is then corked so that the surface of the bromoform rises to the opening of the narrow limb. The tube is then jerked sideways until the concentrate is uniformly distributed through the wide limb. Care has to be taken to prevent the lighter-than-bromoform grains being jerked round the bottom of the tube into the narrow part. After thorough disturbance the tube is held in such a way that the wider limb is vertical and separation is allowed to take place. 'The lighter portion of the concentrate having accumulated at the top of the liquid in the wide part of the tube, the process is repeated until the separation of the heavier-than-bromoform grains in the bend of the tube is complete.'

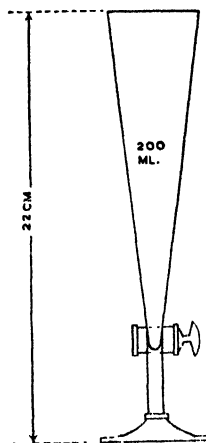


FIG. 7. Spæth Sedimentation Glass.

The tube is held with the narrow end at the left of the operator as he faces it and then slowly turned in an anti-clockwise direction until the narrow limb is vertical with the jet end about $\frac{1}{4}$ in. over a microscope slide.

Choking of the jet by large grains is obviated by pushing in the cork slightly so that a drop falls on the slide. When no more grains can fall down to the jet, the cork is pushed in farther thus expelling two or three more drops on to the slide. The separation is then complete and the minerals ready for drying and mounting.

Another appropriate means is the Spæth sedimentation glass, recommended by A. O. Woodford² (Fig. 7).

Where fused salts are employed separations are most conveniently made in a small test tube, about $\frac{1}{2}$ in. in diameter, the salt and the residue from previous bromoform separation being heated together

¹ *Econ. Geol.*, 23, 1928, p. 99.

² *Econ. Geol.*, 20, 1925, p. 103.

over a bunsen burner or water bath. In either case the heat applied should be the minimum necessary to bring the salt into a clear fluid state, as overheating is fatal. In the fused state, gravitational separation occurs, the lighter particles floating to the surface of the melt, the heavier particles sinking to the bottom. On cooling, solidification ensues, the tube is broken and the 'salt core' cleared of any adhering glass fragments. The core is then split in half across the middle by cutting with a knife and thus the part containing the heavier is separated from that holding the lighter minerals. Each mass is put into a small evaporating dish and the mineral grains ultimately recovered by dissolving the salt in water (unless otherwise

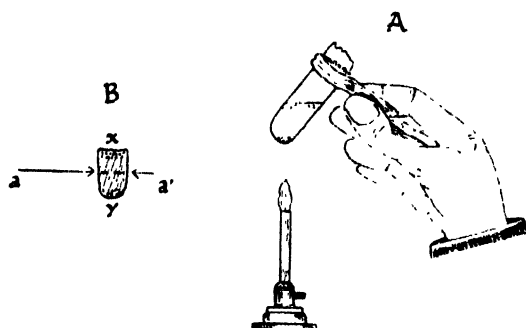


FIG. 8. Diagram to illustrate the use of Fused Salts in Mineral Separation. A, in fluid state with minerals separating out; B, solidified core recovered on cooling; the core is cut along the line a—a', the lighter minerals being held in the part x, the heavier being contained in y.

stated). Fig. 8 taken from *Alluvial Prospecting* serves to illustrate the method¹. With all fused salt separations, manipulation should be as quick as possible to save decomposition and in some cases attack on certain minerals present.

DETRITAL MINERAL CONCENTRATION BY HAND

This very tedious, but often necessary, operation is frequently found in the long run to be the most rapid method of obtaining reasonable concentrates of one particular species from a heavy mineral segregation. Minerals possessing some specific property whereby they can be cleanly selected by physical, mechanical or other means, naturally need no special picking out, but in cases of desired concentrates of such species as epidote, staurolite, pyroxene, etc., especially where these minerals are not very prolific in the

¹ C. Raeburn and H. B. Milner, (Murby, London), 1927.

residue, they will, in ordinary circumstances, have to be isolated by hand. This form of hand-sorting is best carried out with a camel-hair (better still 'sable-hair') brush of fine point moistened with cedarwood oil or glycerine and the segregation is made under the microscope, using low-power magnification and good transmitted light. As picked out, each grain should be placed in a suitable receptacle; a glazed porcelain tile with twelve or sixteen hollows, as employed for colour-testing in quantitative chemical analysis, answers admirably.

A. D. Howard¹ has described a neat pair of tweezers, constructed of two specially prepared brass pins held in a glass tube, having a device which ensures a tight grip on the mineral grain once secured. This instrument is particularly useful in hand-picking detritals and saves much of the fatigue ordinarily accompanying the brush method.

ELIMINATION OF PROLIFIC MINERALS FROM HEAVY RESIDUES

Core-samples, especially those composed of clay and shale and taken from some depth below the surface, frequently present overwhelming quantities of minerals such as pyrite, pyrrhotite, gypsum, etc., which, by masking the less frequently occurring non-opaque species, may render identification and assessment of these a matter of extreme difficulty, so that the residue becomes practically worthless from a petrographic standpoint. Such minerals, once recorded, are best removed; sometimes the initial acid digest does this automatically, but more often than not these minerals find their way into the bromoform residue and have in consequence to be eliminated. It should be noted, however, that in doing so other minerals may be attacked and a mount of the original residue should be made as an initial check.

Anhydrite has a higher gravity than gypsum (2.9-2.98) and where prolific can be removed with hot, strong hydrochloric acid.

Barite. This mineral is liable to give similar trouble, though it is less frequent in occurrence than pyrite and gypsum in petroliferous rocks; it is not uncommon, however, in sediments associated with saline deposits or in porous sandstones of terrestrial origin in which it acts as a cement; or it may be introduced as a heavy drilling mud. Its elimination can be effected by hot concentrated sulphuric acid, in most cases, but the treatment is drastic and may affect other minerals present.

¹ *Journ. Sed. Pet.*, 2, 1932, p. 160.

Cloudy Aggregates attached to certain minerals in the form of a film, thus masking the nature of those minerals, may sometimes be removed by nascent carbon dioxide; any violent effervescence may be equally effective, especially with non-ferruginous compounds such as kaolinite, carbonates, etc. This treatment is not infallible, however.

Gypsum is a frequent constituent of clay and shale and may be very troublesome in oil-well samples. Because of its low gravity (2.3) it should not appear at all in the bromoform residue, though sometimes, owing to abundant inclusions of iron-ore, it does come down with the heavy suite. It is generally eliminated by the bromoform-benzol solution; it may be attacked by hydrochloric acid; drastic treatment consists in digesting with a strong ammoniacal solution of ammonium sulphate.

Pyrite is best removed by digesting the heavy residue with weak nitric acid (up to 15%) or hydrogen peroxide; gentle warming may be necessary. It should be borne in mind, however, that certain other minerals present, e.g. apatite, are liable to attack from this treatment.

Pyrolusite, for the most part exceedingly local in sediments, may if necessary be removed by digestion with strong hydrochloric acid (warm).

Pyrrhotite is soluble in hydrochloric acid and can thus be eliminated. Much of this mineral is, however, destroyed by the first acid digest.

TREATMENT OF ARGILLACEOUS ROCKS

Clay, marl, extremely fine silt and similar material require substantially different treatment for extraction of accessory minerals from that involved in the case of coarser detritus. Some examples, when dry, are extremely difficult to 'break down' under water, though a few drops of ammonia or 10% solution of sodium carbonate may be effective in this respect. P. G. H. Boswell has described a neat method of making the sample practically red-hot and then plunging it into cold water, to obviate the difficulty; but even this is not always successful and very gentle pulverization in a mortar may be necessary. Other methods applicable have already been described (p. 111).

An initial concentration may be obtained by repeated washing with water, in much the same way that panning of sands is carried out (p. 115); the resulting material may have to be cleaned with weak acid, but in many instances this proves unnecessary. When dry, a bromoform separation may be tried and, if the grains are not too small, it may be successful. The author has found, however, that grains of average grade-size < 0.01 mm., will not respond readily to such separation, owing to surface tension or other influences and in such cases recourse has to be made to centrifugal methods (p. 116).

An alternative but tedious way is to mount up several slides of the concentrated material and differentiate where possible under the microscope between the essential and accessory minerals. Elutriation (p. 134) may be resorted to, in order to produce a series of graded crops of minerals which may be mounted for examination under the microscope. It is frequently found that concentrations of heavy minerals occur with two or three definite grades and this facilitates their study, but the method is by no means infallible and will most certainly fail with very fine material. Generally speaking, accessory minerals, as also any detrital quartz present, conform to rather larger grade-sizes than does the clay-substance when pulverized and accordingly it is seldom that one or other of the above methods fails to produce the desired mineral crop.

Shales, mudstones, consolidated marls and similar fine, compact rocks, are treated as crushed samples according to the methods described on p. 127.

TREATMENT OF CALCAREOUS ROCKS

The extraction of heavy mineral residues or of any detrital mineral components from limestones and allied types is not a difficult matter and proceeds either according to the methods described for crushed rocks (p. 127), which is usual, or alternatively acid solubility (p. 257) is employed and detrital constituents separated with bromoform from the inorganic residuum, preferably with the centrifuge; this last method applied more particularly to soft limestones, oozes and similar materials; most calcareous rocks are hard and compact and need a degree of crushing before they can be treated for mineral concentrates. After acid-treatment of limestones it is often desirable to wash the residue thoroughly to remove clay material, as the latter impedes bromoform separation.

TREATMENT OF CARBONACEOUS ROCKS

The microscopy of coal usually concerns nature and origin of vegetable structures or coal-substance and, as such, lies outside the scope of sedimentary petrology. Consequently few but palaeobotanists are inclined to probe coal-sections deeply; mineralogical evidence is subsidiary to the more fundamental study of the hydrocarbons. Coal may, however, yield heavy mineral assemblages at least as definite and varied as those obtained by panning clays, for instance; not merely ubiquitous pyrite or marcasite, but the more stable detrital constituents may be released by combustion or solution of the organic matter. This phase of investigation was first suggested to the author by the late W. W. Watts many years ago,

since when experiments have been made from time to time on various coals (including lignite) and coal-ash, with interesting though possibly limited results.

The coal substance may be eliminated by burning the coal to ash, washing (by which means much of the light 'flaky' matter is disposed of) and drying, then examining microscopically the residue, which may be further concentrated by bromoform if desired. The high temperature of combustion is, however, liable to destroy certain minerals. Alternatively the solution method, using aqueous caustic potash, pyridine, phenol, chloroform or sodium hypochlorite has been successfully employed with different types of coal, though some varieties are stubborn (hard bituminous coal and anthracite); gentle pulverization before solution is necessary.

The average inorganic residue (ash) of coal is seen to consist of quartz (often iron-stained), black particles of metallic ore (some of the latter possibly unburned or undissolved carbon), scaly micaceous matter and stable accessory minerals such as tourmaline, garnet, zircon, rutile; such minerals sometimes resemble those extracted from associated ganisters or grits, or may be quite different, a point of some theoretical significance; other samples have yielded zinc and copper ores.

On searching the literature we find that O. Stutzer¹ records occurrence of millerite, cinnabar, chalcopyrite, sphalerite, galena, malachite and molybdenite in coal; gold has been found in the coal of Cambria, Wyoming²; silver has been observed in black carbonaceous shale³; vanadium occurs in coal-ash from Scotland⁴, in peat-ash from North Carolina⁵, in lignite from San Rafael, Mendoza, Argentine⁶ and in coal from Yauli, Peru⁷; uranium was detected by A. E. Nordenskiöld in an 'anthracite bitumen' from Sweden⁸ and by H. Liebert in the 'Kolm' of that country⁹ as it has since been in coals from many other countries; radium has been discovered in certain Alabama coals¹⁰; germanium and gallium have been found in various British coals¹¹. Although in some of these cases the elements have only been detected during the course of quantitative chemical analysis, the records clearly indicate possibilities of mineralogical interpretation by microscopical examination.

¹ Kohle (Allgemeine Kohlengologie), Berlin, 1914, pp. 19, 193.

² R. W. Stone, *U.S. Geol. Surv., Bull.*, **499**, 1912, p. 63.

³ T. A. Rickard, *Trans. Amer. Inst. Min. Eng.*, **26**, 1896, p. 978.

⁴ J. C. H. Mingay, *Rec. Geol. Surv. N.S. Wales*, **7**, 1903, p. 219.

⁵ C. Baskerville, *Journ. Amer. Chem. Soc.*, **21**, 1899, p. 706.

⁶ J. J. Kyle, *Chem. News*, **66**, 1892, p. 211.

⁷ *Journ. Chem. Soc.*, **70**, 1896, pt. ii, p. 252. ⁸ *Comp. Rend.*, **116**, 1893, p. 677.

⁹ C. Winkler, *Zeitschr. Kryst. Min.*, **37**, 1903, p. 287.

¹⁰ S. J. Lloyd and J. Cunningham, *Amer. Chem. Journ.*, **50**, 1913, p. 47.

¹¹ G. T. Morgan and G. R. Davies, *Chem. and Ind.*, **59**, 1937, p. 717.

Geologically, significance of petrography of coal attaches to possible indication afforded of its mode of origin; detrital constituents when localized may suggest direction of transport, hence 'drift coal' or '*growth-in-situ*' may be indicated either by impoverishment or absence of such minerals or by close resemblance of an assemblage to that of intimately associated measures. The potentialities of this phase of petrographic work are obvious, but too much must not be expected of it, especially with bituminous and anthracitic coals. Terrestrial peat, certain lignites and brown coals and especially estuarine coals, form the most encouraging materials to work on. For further data, see Vol. II, Ch. II.

Oil-shales, asphaltics, asphaltic rocks and various bituminous substances are similarly interesting, the mineral accessories extracted often being sufficiently well individualized to warrant their use as indices of provenance of the material, direction of flow of the bitumen, manner of impregnation and so on. From another standpoint, the presence of traces of certain minerals or elements in such substances may attest the action of bacterial or other organisms possessing specially selective or segregative powers, thus throwing light on the complicated mechanism of the genesis of these substances; vanadium minerals in Trinidad '*manjak*' and in the '*grahamite*' of Page, Oklahoma, are cases in point.

TREATMENT OF BITUMINOUS IMPREGNATED ROCKS

Oil-saturated sands, if the hydrocarbon is in a fluid state, can be clarified by repeated digestion of the sample with cold (sometimes warm) benzol, chloroform, ether, carbon disulphide, or trichloroethylene. If, however, impregnation is of a solid asphaltic character, an extraction process must be carried out such as described in Chapter VII, p. 265. In no circumstances should a sample containing petroleum or asphalt be proceeded with for heavy mineral separation unless such extraction has been carried out, as the presence of hydrocarbon will discolour and render useless not only bromoform-benzol solution but bromoform itself; recovery of such contaminated bromoform is a very long and uneconomic process; the hydrocarbon also tends to coat individual particles, thus rendering their identification almost impossible. A further difficulty results from the tendency of such impregnated rocks to flux with Canada balsam during the process of making the microscope slides (p. 91).

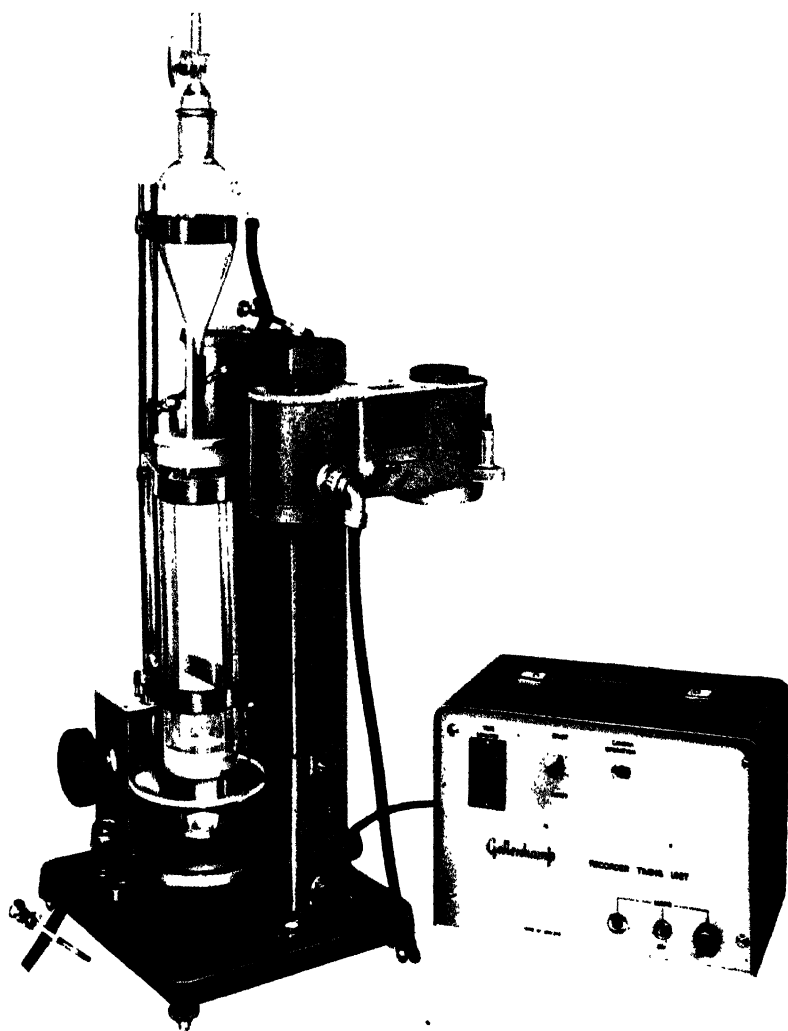
TREATMENT OF CRUSHED ROCKS FOR HEAVY MINERAL SEPARATION

Compact, consolidated sediments such as sandstones, grits, quartzites, shales, mudstones, ironstones and the like, are normally

studied by means of thin sections cut from the samples, as with igneous rocks. But just as the minor accessory minerals frequently escape detection in thin sections of the latter, so it is with sedimentary types and for this reason the supplementary practice of microscopical examination of the crushed material is often, where appropriate, carried out.

The methods, applicable alike to igneous, metamorphic and sedimentary rocks, consist in crushing the sample in a steel mortar until pulverized, avoiding formation of rock-flour as far as possible. The powder is then panned (p. 114) in water in a 10 in. evaporating basin and in this way the finer light material may be eliminated and the heavier fragments concentrated at the bottom of the basin. As it is often necessary to treat several pounds of rock before an adequate concentrate is obtained, repeated panning is resorted to, using more than one dish at first, but gradually reducing the quantity of material until it can all be concentrated in one receptacle. Panning is, of course, inadmissible in quantitative work; in such a case, the powder is poured into a beaker of water, stirred, then allowed to settle; the water is decanted and the process repeated until the liquid decanted is clear. Thus obtained, the concentrate or powder is dried in the usual way and then submitted to a bromoform separation to isolate the heavier constituents. If the authigenous material is such as to mask the character of the fragments, clarification by means of dilute acid is carried out as previously described.

Much intensive research has been and still is being conducted on accessory minerals of granitic and associated rocks, with important results bearing both on their genesis and on their influence as contributors to sedimentary formations. This work follows particularly the lead of A. Brammall and H. F. Harwood in their exhaustive study of the Dartmoor Granite, to which reference is made elsewhere (Vol. II). The technique implied follows closely that outlined in the preceding paragraph on crushed rocks and consists in pounding up several lumps of the rock, panning off the light powdery material ("flour") produced, except in quantitative work (see above), thus gradually reducing the bulk until it is of reasonable size for bromoform concentration in the usual way. Thereafter various methods are employed for isolation of particular mineral species and these minerals are then accorded detailed individual study, both for their own sake and also for the evidence they furnish of geochemical conditions attending conception and consolidation of the granite. Further reference to this work and to its significance in sedimentary petrological studies will be found in Vol. II, Ch. IV, also in the Bibliography (Vol. II).



GALLENKAMP SEDIMENTATION BALANCE WITH AUTOMATIC RECORDING
(Courtesy of Gallenkamp & Co., Ltd., London, E.C. 2)

CHAPTER IV

LABORATORY TECHNIQUE PART 2. MECHANICAL ANALYSIS OF SEDIMENTS AND DETERMINATION OF PARTICLE SIZE DISTRIBUTION¹

Mechanical Analysis—Air Permeability (Specific Surface)—
Centrifugal Sedimentation—Elutriation—Sedimentation—Sieve
Analysis—Miscellaneous Methods of Particle-Size Determina-
tion—Geological (Petrological) Classification of Sedimentary
Rock-Particles—Expression of Results of Mechanical Analyses
—Fineness Modulus—Appendix: On Particle-Size and Micro-
scopical Measurements.

*

MECHANICAL ANALYSIS

MECHANICAL analysis is recognized laboratory technique for determination of individual or aggregated particle-size and also particle-size distribution of constituent mineral grains of a sedimentary rock, whether consolidated or incoherent. Its applications are not of course confined to natural sediments, but embrace all cases of crushed rock, igneous as well as sedimentary, and artificial materials.

The fundamental objects of mechanical analysis are threefold; (a) to establish individual particle-sizes, (b) to ascertain relative proportions (by weight) of particles occurring within certain prescribed size-limits, hence particle-size distribution, and (c) to interpret results of such analyses in a manner and in terms which will present a true numerical or graphical record of the mechanical, as distinct from mineralogical, constitution of the rock or material concerned.

There are several methods, old and new, now available for carrying out mechanical analyses leading directly or indirectly to particle-size evaluation and classification. Choice of procedure depends

¹ In the 3rd edition of this book (1940), this chapter (IV) on mechanical analysis of sediments was contributed by L. J. Chalk, M.Sc., F.R.I.C., F.Inst.Pet., formerly Chief Chemist, Geochemical Laboratories. In the present chapter, much of the text has been re-written and brought up to date; it is the joint work of A. H. Clarke, M.Sc., F.R.I.C., Assoc.F.Inst.Pet., Chief Chemist, Geochemical Laboratories, and the author.

largely on nature and inherent coarseness or fineness (grain-size) of the material under investigation. Arranged alphabetically, these methods include:

- (a) Air Permeability (specific surface) p. 130.
- (b) Centrifugal Sedimentation (p. 132).
- (c) Elutriation (p. 134).
- (d) Sedimentation (p. 148).
- (e) Sieve Analysis (p. 164).
- (f) Miscellaneous (p. 175).

Broadly speaking, method (a), Air Permeability, means specific surface measurements and applies not only to Portland and other cements within mandatory size-ranges specified in this country, U.S.A. and elsewhere, but equally to many natural and synthetic mineral powders. Method (b), Centrifugal Sedimentation, concerns materials containing substantial proportions of particles below 5μ , often wholly below 2μ . Elutriation (c) is the time-honoured procedure for classifying particles $< 50\mu$ (lower limit 10μ) by upward stream of water or other liquid; also air currents in special apparatus (air elutriation) may be used for classifying dry powders between 40μ and $>2\mu$. Method (d), Sedimentation, depends on initial dispersion and ultimate suspension of the powder to be classified, particle-size being indirectly determined by measurements at fixed points in the suspension at selected intervals of time; particle-size assessment down to 0.2μ or less is possible by this process (which includes among other techniques the well-known Pipette Method). Sieve Analysis (e) is, of course, the commonest and most popular direct method of laboratory classification of stones, crushed rock and smaller particles, dry or wet, ranging usually from an upper limit of about 4 in. in nominal size down to about 0.05 mm., the latter generally considered to be the practicable lower size-limit attainable by this means. In the miscellaneous division (f) are grouped 'unconventional' but none the less significant, modern techniques devised for particle-size analysis.

AIR PERMEABILITY (SPECIFIC SURFACE)

This is an indirect method of test for fineness of powdered material adapted successfully for ordinary Portland or rapid-hardening cement, in terms of specific surface, conventionally expressed as 'total surface area in square centimetres per gramme'¹. It is important to understand that determination of specific surface is not a *direct* means of ascertaining particle-size distribution in a sample. On the contrary, it is basically an area measurement per gramme

¹ B.S.12 : 1958, App. A, p. 11. See also Ch. VII, p. 294 (this volume).

of a mass of particles, large and small, from which, however, some idea of overall fineness of the sample may be assessed.

Theoretically, specific surface, S_w , in terms of area per unit weight, is related to surface mean diameter of spheres, d_{vs} , by the equation¹:

$$d_{vs} = \frac{6}{S_w P}$$

where P is the density of the spheres.

'While the proportionality factor is greater than 6 for particles other than spheres or cubes, the factor 6 is usually considered to be sufficiently close to the correct value to give an adequate representation of the size'¹. For extended discussion on this subject, see reference¹.

One form of apparatus commonly employed in this country for surface-area measurement is figured in B.S. 12 : 1958 (p. 29). In the U.S.A., what is known as the 'Blaine Air Permeability Apparatus' is used², and both apparatus and principle of the test are somewhat different from the B.S. method³. Full details of procedure in both cases are given in the appropriate references below; also U.K. procedure and calculations are summarized in Ch. VII of this volume.

Formerly a sieve test was employed for determining fineness of cement, permitting a maximum of 10% retained on a 170 mesh B.S. sieve for ordinary, and 5% retained for rapid-hardening cement⁴. Sieving was deleted from the later specification (1958) and specific surface measurement substituted, so that minimum fineness for ordinary Portland cement is now 2,250 sq.cm./g. and for rapid-hardening cement 3,250 sq.cm./g. A.S.T.M. requirements for minimum average specific surface in sq.cm./g. are higher and range from 2,800 to 3,200 sq.cm./g., according to type of cement involved⁵.

This method of approach to fineness is not commonly employed with natural rock-powders, fine-grained sediments or mineral powders *in the field of normal petrographic research*, but it is widely used in industry and would appear to have decided potentialities in circumstances where classification of finely-divided natural sediments whose particle-size range lies substantially below 90 μ is sought, and where, particularly, *determination of mean particle-*

¹ R. D. Cadle, *Particle Size Determination*, (Interscience, New York), 1955, VIII, p. 239 and refs. cited, pp. 262, 263.

² A.S.T.M. C204-51, p. 129.

³ F. M. Lea, *The Chemistry of Cement and Concrete*, 2nd ed., (Arnold, London), 1956, pp. 317-333.

⁴ B.S.12 : 1947.

⁵ F. M. Lea, *op. cit.*, p. 318.

diameter value is a more important function than particle-size distribution. In the chemical industry, for instance, apart from properties of matter concerned with specific surface, such as behaviour as an adsorbent, *e.g.* cement as above described, surface-area measurements are commonly sought for determination and control of rates of chemical reactions.

To illustrate petrographic research possibilities, an improved apparatus for rapid determination of surface area of mineral powders and of their mean pore radius, by air-permeability technique, applicable to material within the range 40μ – 0.4μ , was originally described by P. J. Rigden¹; it is listed by Griffin & George Ltd.² This apparatus possesses decided advantages in that it is relatively inexpensive, and adaptable for routine control of fineness of both natural and manufactured materials, obviating the need for the more time-consuming methods of assessing complete particle-size distribution. Among the list of natural and synthetic products for which it can be used may be quoted:

(1) Sands, clays, pigments and other powdered materials used in the refractory and ceramic industries.

(2) All types of filler for bituminous materials, *e.g.* powdered limestone, granite, slate, etc.

(3) Portland cement, magnesium phosphate, lime, etc., for the building and flooring industries.

(4) Powdered metals of all kinds.

(5) Powdered coal and pitch and other fuels.

(6) Titanium dioxide, zinc oxide, lithopone, carbon black and other pigments used in the paint and rubber industries².

The apparatus is a modification of the Lea-Nurse method³ by P. J. Rigden and is suitable for powders of specific surface between 500 – $50,000$ cm.²/g., *i.e.* 40μ – 0.4μ , assuming S.G. of 3.

CENTRIFUGAL SEDIMENTATION

Variations in centrifugal methods for particle-size classification in finely-divided sediments have been described by many workers in this field for several years past⁴. The common goal among

¹ *Journ. Soc. Chem. Ind.*, **62**, 1943, p. 1.

² Catalogue 56S, 1956, p. 496.

³ P. C. Carman, *Journ. Soc. Chem. Ind.*, **57**, 1938, p. 225; **58**, 1939, p. 2; F. M. Lea and R. W. Nurse, *Journ. Soc. Chem. Ind.*, **58**, 1939, p. 227. See also Symposium on Particle Size Analysis, *Supp. Trans. Inst. Chem. Eng.*, **25**, 1947, p. 47.

⁴ T. Svedberg and J. B. Nichols, *Journ. Amer. Chem. Soc.*, **45**, 1932, p. 2910.

P. D. Trask, *Econ. Geol.*, **25**, 1930, p. 581.

C. E. Marshall, *Mineralogical Methods for the Study of Silts and Clays*, *Zeitschr. Kristallogr.*, **A**, **90**, 1935, p. 8.

them has been reduction of the inordinate amount of time taken by ordinary sedimentation processes (p. 159) to separate material of the order 1μ and below. For example, quartz grains (S.G. 2.65) of diameter 1μ take 31 hours to settle 10 cm. in water at 20°C ; 0.5μ grains require 124 hours under the same conditions; 0.1μ particles will take as long as 130 days. Admittedly the time factor can be cut by shortening the settling distance, but this often introduces other difficulties. Centrifugal sedimentation aids considerably in overcoming this disadvantage, although both technique and interpretation of results may prove somewhat more complicated than, for example, the simpler pipette method (p. 158).

The theoretical aspect of particle-size determination applicable to practically any method making use of a centrifuge has been discussed by T. Svedberg, who developed a modification of Stokes' equation (p. 135) as follows:

$$d = \frac{6}{\omega} \sqrt{\frac{\eta \log_e \frac{s_2}{s_1}}{2(\rho - \rho')t}}$$

where d = particle diameter, s_2 = distance from axis of rotation to bottom of centrifuge tube, s_1 = distance of that axis to meniscus of suspension, ω = angular velocity, ρ = particle density, ρ' = density of suspending medium and t = time.

For any particular experimental conditions, that equation can be reduced to:

$$d = k/\sqrt{t}$$

where k is a constant¹.

Gravitational methods of particle-size determination, e.g., sedimentation (p. 148), are restricted for all practical purposes to material of the order of 2μ lower limit. With centrifugal accelerations, T. Svedberg and others developed a force of 750,000 times that of gravity, using the 'Ultracentrifuge'². This introduced a new conception of what is practicable with this technique. Normally with laboratory centrifuges specially designed for particle-size classification, a range of 2μ down to 0.05μ can be realized. Various models are available to suit specific requirements and in the United Kingdom certain manufacturers specialize in this type of apparatus³. High-speed bucket types are generally favoured,

¹ R. D. Cadle, *op. cit.*, p. 228. See also J. K. Donoghue and W. Bostock, *ref. on p. 134*.

² T. Svedberg, *Ind. Eng. Chem., Anal. Ed.*, **10**, 1938, p. 113. T. Svedberg and K. O. Pedersen, *The Ultracentrifuge*, (Oxford Univ. Press, London), 1940.

³ Gallenkamp-Towers, London, E.C.2.

Griffin & George, Ltd., Wembley, Middlesex.

Sharples Process Engineers, Ltd., London, S.W.7.

where maximum speed (fully loaded) may range up to 13,000 r.p.m. (equivalent to R.C.F. value of 20,000 g.).

The 'Sharples Super-Centrifuge' laboratory model, a rotating hollow cylinder type, with electric drive, maximum speed 23,000 r.p.m. and C.F. 13,200 g., or the turbine, compressed air or steam driven, model, by the same makers, attaining a maximum speed of 50,000 r.p.m., with maximum C.F. 62,000 g., are also much used for this kind of work¹.

A comparative newcomer is the 'Gallenkamp Centrifugal Sedimentometer'. This apparatus is the outcome of research in the Simon-Carves research laboratories at Cheadle Heath, Stockport, and embodies a new technique for particle-size analysis by centrifugal sedimentation². It can classify material within the range 0.1–5 μ . 'The apparatus consists of a 2-speed centrifuge fitted with a special conical head holding a homogeneous suspension in a suitable liquid of the sample under examination. On rotating the head, particles are deposited by the centrifugal force on to a series of collecting strips placed at various distances from the axis of rotation. The particle-size distribution is calculated from the fractional weight of the sample deposited on the various strips. The running times are adjusted to cover particular size-ranges and usually lie between 15 and 120 mins.'³. In calculating particle-size distribution as sought with this sedimentometer, density and weight concentration of the sample under examination, density and viscosity of the liquid employed, dimensions of apparatus and operation time, must all be known.

Another type of apparatus for particle-size analysis, embodying the principle of centrifugal pipette sedimentation, having a range of 2 μ –0.1 μ , has been described by H. J. Kamack⁴. With this, which is analogous to the Andreason pipette method (p. 158), it is possible to use 'withdrawal' pipettes for examination of contents while the centrifuge is actually in motion.

ELUTRIATION

Elutriation is a laboratory process whereby classification of particle-size is effected by means (generally) of an upstream of fluid which may be air (dry elutriation) or water (wet elutriation). Elutriation is thus the reverse of sedimentation (p. 148), where the

¹ E. A. Hauser and C. E. Reed, *Journ. Phys. Chem.*, **40**, 1936, p. 1169; E. A. Hauser and H. K. Shackman, *Journ. Phys. Chem.*, **44**, 1940, p. 584; E. A. Hauser and J. E. Lynn, *Ind. Eng. Chem.*, **32**, 1940, p. 659.

² J. K. Donoghue and W. Bostock, *Trans. Inst. Chem. Eng.*, **33**, 1955, p. 72.

³ Gallenkamp-Towers (London), *General Catalogue*, 1960, p. 649. (Note. Since going to press we are informed by Messrs. Gallenkamp that their Centrifugal Sedimentometer is no longer in production.)

⁴ H. J. Kamack, *Anal. Chem.*, **23**, 1951, p. 844.

fluid medium is static and particle settlement is determined gravitationally or may be urged by centrifugal methods (p. 132).

The fundamental concept on which elutriation (also sedimentation) is based is the principle embraced by Stoke's law, which relates rate of fall of a *spherical* particle to diameter of that particle; this may be expressed by the equation:

$$d = \sqrt{\frac{18\eta U}{(\rho - \rho')g}}$$

where d = diameter of particle, η is the viscosity of the fluid, U = rate of fall, ρ = density of the spherical particle, ρ' = density of the fluid involved, and g = acceleration of gravity.

It is this equation which is normally used to interpret elutriation results in terms of a factual particle-size distribution in a given sample. The sub-sieve fraction 50μ and downwards to 10μ , is the operative range in which elutriation can be most profitably utilized, but with some elutriators $>50\mu$ material is frequently isolated if conditions of test warrant such convenient extension.

It is important to realize that Stoke's law concerns *spherical* particles only and that its validity is sustained when resistance to movement of a particle is fundamentally due to viscosity of the medium concerned. There are practical limitations to its application which are clearly stressed by R. D. Cadle¹.

The assumption is 'that the sphere is smooth and rigid and that no slipping takes place over its surface, but also that it is placed in a medium of unlimited extent and is unhindered in its fall. Most sediments are not composed of spheres, neither are the surfaces of the particles smooth, while the extent to which their fall is influenced by the presence of other particles or the walls of the containing vessels depends largely on the design of the elutriator. Anomalous results are, therefore, to be expected when one dimension of the particle differs considerably from the other two. For instance, it would be possible so to adjust the overflow velocity that a flat particle could be overflowed and a spherical particle of equal mass and density would sink. For this and other reasons stated below, it is advisable to examine all elutriation fractions microscopically'.

'Perfect size classification cannot be expected with any elutriator since, although it is theoretically possible to keep a single particle suspended indefinitely with a certain rising current velocity, or to overflow the particle by slightly increasing the velocity, in actual practice particles are hindered in their motions by the presence of numerous other particles'.

¹ *Op. cit.*, p. 199.

'Variation in the temperature of the medium will result in a change in its viscosity and density and consequently in the size of particle overflowed. *Elutriation is, therefore, carried out at constant temperature* or alternatively the velocity is altered from time to time to compensate for changes in temperature. The viscosity of water at 20°C. changes by approximately 2% for a 1°C. rise or fall, from which it is evident that change in viscosity is of far greater importance than change in density.'

'Size classification by means of elutriation cannot be carried out with heterogeneous samples consisting of particles of different densities as with a given velocity of overflow, the higher the density of the particle, the smaller the diameter overflowed. In a majority of sediments this consideration may be neglected, but where substantial amounts of heavy minerals are present, the sample should be separated before elutriation into crops of different specific gravities and each crop elutriated separately'¹.

Normal procedure with elutriating sediments is to use progressively accelerated fluid velocities, whereby the sample treated is separated into fractions of increasing particle-size. Each fraction thus obtained is segregated by filtration or other means, dried and weighed, thus giving the required size-distribution, which, based on Stoke's equation, involves *predetermined* size limits, e.g. 50 μ –10 μ for silt fraction and below 10 μ for clay or mud fractions. From a practical standpoint, however, classification of <10 μ particles is best achieved by ordinary sedimentation methods (p. 148) or by centrifugal sedimentation technique (p. 132).

In any interpretation of size-analyses of sedimentary rock particles in terms of geological, more especially petrological, nomenclature, the logical corollary to any form of mechanical analysis, recourse must be had to certain conventional classifications which, since they embrace the coarsest materials as well as sub-sieve particle-sizes, are more comprehensively considered in a later section specially devoted to this aspect of the subject (p. 178). We therefore proceed to describe briefly the more important types of apparatus available for dry and wet elutriation.

The arrangement is purposely alphabetical, so as not to appear to favour one type more than another; the student will soon find from experience that each problem of particle-size analysis brings with it certain theoretical and practical *desiderata* which only a sound unbiassed knowledge of all available facilities will satisfy. One is frequently faced with the prospect of a full-scale particle-size analysis of a natural sediment which involves not simple procedure but a combination of sieving, elutriation, sedimentation, micro-

¹ This and the three preceding paragraphs in parenthesis, are taken from *Sedimentary Petrography*, 3rd ed., Ch. IV, pp. 96, 97, by L. J. Chalk.

scopical investigation and other highly specialized techniques, before the whole project is carried to a satisfactory conclusion. It is strongly recommended, especially to the beginner, that such data as are recorded below be amplified by appeal to original references cited, before final selection is made of the most suitable apparatus for the particular job in hand.

AIR ELUTRIATORS

It is a cardinal principle with air elutriation that the air itself is used absolutely dry. This can be achieved by passing it through silica gel or activated alumina.

Gonell Air Separator. This is what is known as a 'down-blast' type of air-elutriator and has been widely used for cement particle-size analysis in Europe. It is a somewhat complicated but quite efficient piece of apparatus, details of which will be found in the reference below¹.

Mayntz Petersen Fluorometer. This is an 'up-blast' type of elutriator consisting of a vertical tapering glass vessel (Fig. 9A), approximately 4 ft. long and 4 in. maximum diameter (top half), connected at the bottom apex via a 3-way tube to a manometer and electric motor-driven blower. Air enters at the bottom of the elutriator column and, once flowing, a 5 g. sample of the material to be separated is transferred to the interior of the vessel, care being taken not to touch the sides. After about 15 min. the blower is stopped and the coarse residue weighed. Percentage loss in weight is termed 'flour', particle sizes being checked microscopically or by other means. Air pressure most suitable for this apparatus is ascertained by previous trial with a sample of known flour content² produced by a standardized instrument³.

F. M. Lea has commented in the case of cement: 'the up-blast type of air elutriator has the disadvantage that choking is apt to occur, and, which is more troublesome, the air tends to force open "pipes" through the cement and to leave part of it unagitated'⁴.

Pearson Air Elutriator. This is another 'down-blast' type of elutriator, air being blown into the apex of an inverted cone (Fig. 9B).

¹ H. W. Gonell, *Zeit. Ver. Deutsch. Ing.*, 72, 1928, p. 945, and *Zement*, 17, 1928, pp. 1786, 1819, 1848.

² Flour content is generally understood to represent the amount of fines carried over by elutriating a known weight of the sample for a fixed time in an air-stream of known velocity.

³ *Sedimentary Petrography*, 3rd ed., 1940, p. 105.

⁴ *Op. cit.*, p. 322.

It has been chiefly employed for cement classification, but is obviously adaptable for other powdered materials. With this apparatus, an air-speed of 21 ft./min. and a water pressure of 41.5 in., gives a separation of 34μ particle-size. Again, it is usually percentage of flour in the cement sample which is the aim of the experiment. F. M. Lea states: 'the value obtained, . . . while very useful for comparing different cements, is somewhat arbitrary, as some further loss occurs if the blowing is continued for a longer period' (than 25 min.)¹. Details of design and operation are given by that author.

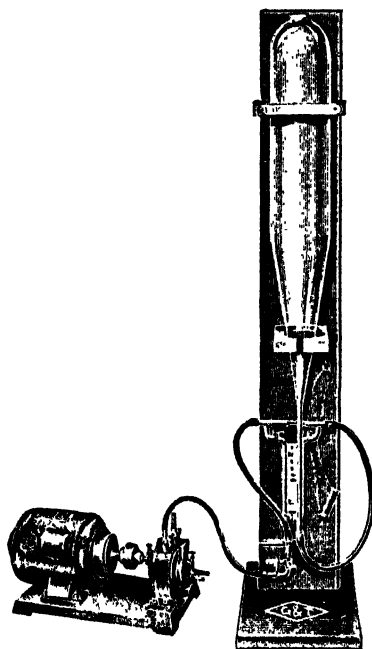


FIG. 9A. Mayntz Petersen Flourometer.

Roller Particle Size Analyser. This particular apparatus is popular in the United States and is suitable for separating commercial rock-powders, e.g. limestone, pumice, slate, metals, etc., into well-defined fractions, subsequently subjected to microscopical check. R. D. Cadle has described and figured this elutriator and its mode of operation in detail. He says 'it consists of an air jet inlet, a U-shaped Pyrex glass vessel which holds the sample of

¹ *Op. cit.*, p. 323; see also J. C. Pearson and W. H. Sligh, *Bur. Stand. Tech. Paper*, 48, 1915.

powder, oscillation connections for the glass vessel, 4 stainless steel chambers, a collector for the sized fractions and a Pyrex gooseneck connector. The apparatus is equipped with a meter for determining the rate of flow of the air. The 4 settling chambers are 9 in., $4\frac{1}{2}$ in., $2\frac{1}{2}$ in., and $1\frac{1}{8}$ in. in inside diameter. The collector is an extraction thimble¹.

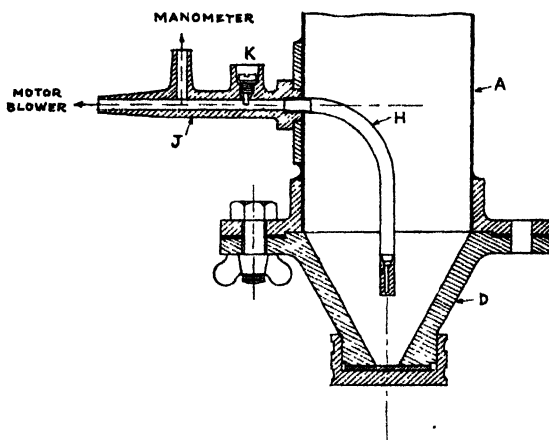


FIG. 9B. Air Elutriator (after F. M. Lea).

A -- brass tube 4 ft. long, 4 in. diameter. D -- air-tight brass cone.
H -- nozzle. J -- oil trap. K -- adjusting screw for calibration of air-inlet tube.

It is customary to operate on sub-sieve 44μ and less particle-size material for this method of analysis and counting residue in the U-tube after the run, a total of five fractions of different size-limits should be obtainable. 'Each fractionation requires from ten to sixty minutes before the point is reached at which further loss becomes negligible. An accuracy of $\pm 0.2\%$ in the weight of different size-fractions has been thus obtained'².

For other patterns of air elutriators, further references should be consulted³.

¹ *Op. cit.*, p. 232; see P. S. Roller, *Journ. Amer. Ceram. Soc.*, 20, 1937, p. 167; also R. N. Traxler and L. A. C. Baum, *Determination of Particle Size Distribution in Mineral Powders by Air Elutriation*, *Rock Products*, 37, 1934 (6), p. 44.

² F. M. Lea, *op. cit.*, p. 322. Note: The Roller Analyser is available commercially from the American Instrument Co., Inc., Silver Spring, Maryland.

³ H. E. T. Haultain, *Trans. Can. Inst. Min. Met.*, 40, 1937, p. 229; J. M. Dalla Valle, *Micromeritics*, 2nd ed., (Pitman, New York), 1948.

WATER ELUTRIATORS

These imply use of water or in certain circumstances other fluids (*infra*) for up-stream separation of particle-sizes in accordance with principles underlying Stoke's law previously discussed in this chapter (p. 135). Water elutriation takes longer than air separation. It has an advantage over the latter, however, when the nature of the material to be analysed 'undergoes a grinding action in the air stream or resists dispersion in the air'¹. Elutriators of the 'wet' class range from the single vessel type (p. 147) to multi-tube separators having certain practical advantages as explained later. For rapid and accurate work, the 'kinetic' type elutriator is most valuable, especially in industry where routine mechanical analyses of sediments of finely powdered products may be involved almost daily.

Elutriation must always be carried out at the same temperature if consistent and comparative results are to be realized.

Andrews Kinetic Elutriator. This is the modern version of the kinetic laboratory elutriator², for a long time successfully employed in the author's laboratories with many different sedimentary rock-powders. It is capable of division of 5-50 g. samples of fineness down to 10μ into three grades in 2-3 hours. Apart from natural sediments it has been used for crushed mineral ores, ceramic and refractory products, pulverized fuels, pigments, oxides, etc. (with water), also cements and plasters (with white spirit, petrol or other fluids inert to these materials, subject to certain modifications in construction of bungs, glass stopcocks, etc.).

The apparatus (Fig. 10) is self-explanatory. Alphabet references in the diagram are as follows:

- | | |
|---------------------------|---|
| A. Air vent | K. Tap |
| B. Feed tube | L. Lower vessel |
| C. Piezometer tube | M. Graduated vessel |
| D. Lower air vent | N. Tap |
| E. Tube | O. Outlet |
| F. Cone | P. Tap |
| G. Hollow central fitting | R. Thermometer |
| H. Top classifier | S. Buchner funnel with filter paper |
| J. Opening and clip | T. Thermostatically controlled heating bath |

The above items may usefully be annotated: Feed tube B is a constant head unclassified feed controlled by surface tension. Tube E is

¹ R. D. Cadle, *op. cit.*, p. 232.

² L. Andrews, Elutriation as an Aid to Engineering Inspection, *Proc. Inst. Eng. Insp.*, **25**, 1927-28; Symposium on Particle Size Analysis, *Inst. Chem. Eng.*, London, 4 February 1947, p. 114. *Note:* This apparatus can be obtained from International Combustion, Ltd., London, or from Griffin and George, Ltd., Wembley, Middlesex.

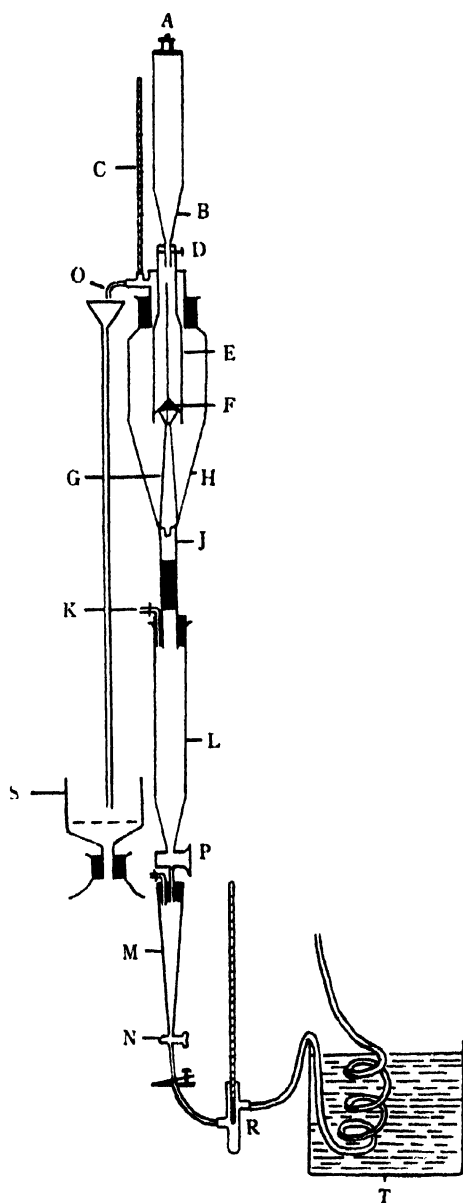


FIG. 10. Andrews Kinetic Elutriator.

also unclassified feed. The upper part of the top classifier H is filled with finely-divided particles borne upwards by rising water-stream. The stationary cone F acts as a buffer against which particle aggregations are disassociated by high velocity impact. The lower vessel L is a classifier of coarse and intermediate particles. The removable graduated vessel M acts as a measuring tube.

The following guide to procedure with this elutriator is based largely on experience with its operation in the author's laboratories and is quoted verbatim from the original and extremely lucid description by L. J. Chalk¹.

'The feed-tube B is removed and a small stopper placed in the bottom. The sample (10 g.) which has previously been dispersed by boiling with water for 5 minutes, is then introduced, after which the feed tube is completely filled with water, the top stopper inserted and the air vent closed. The elutriator is allowed to fill with water until it overflows from the jet and the feed-tube is inserted after removing the small stopper. The air vent D is opened and the level of the water allowed to rise and submerge the bottom of the feed tube. The sample then commences to fall into the main classifier in a slow and even stream. When it has been displaced from the feed tube, the air vent A at the top is opened and the water allowed to run from the feed tube into the classifier, after which the vent is reclosed. The sample falls past the annular opening between the tube E and cone F and sinks to the bottom of the classifier, whence it passes up the hollow central fitting G, strikes the underside of the cone F and passes to the overflow. A piezometer tube C indicates rate of flow.'

'For separation of the $<10\mu$ fraction the flow of water issuing from the outlet of the elutriator is adjusted with a measuring cylinder and a stop watch to that shown in the tables accompanying the instrument as necessary to separate particles up to 10μ in diameter (1.5 ml. per second). For this particular separation the entire central fitting can with advantage be omitted, as at this velocity no impact takes place against cone F and the presence of the fitting merely obstructs the opening at J. It is not easy to judge the end-point of separation from the appearance of the liquid in the classifier H and for precise work it is preferable to continue elutriation until not more than 0.2% by weight of the original sample is overflowed in two hours. The time taken for this separation is dependent on the nature and proportion of fine material present in the sample; in certain instances it may be as long as forty hours.'

'The amount of $<10\mu$ material may be determined (1) by passing the overflow direct to a previously dried and weighed filter paper on a Buchner funnel S, filtering under slight suction and subsequently drying to constant weight; (2) by difference, after filtering, drying and weighing the material left in the elutriator; or (3) by difference, without removing the material left in the elutriator but by weighing all

¹ *Sedimentary Petrography*, 3rd ed., 1940, pp. 98-103.

subsequent overflows and residues. Method (2) is usually most satisfactory, although it involves re-dispersion of the residue if further fractions are to be separated. It is not advisable to attempt to collect the overflows in large bottles, decant off the water and weigh the residue, as loss invariably occurs when this practice is followed.'

'The following modification of method (2) has been found satisfactory. The residue in the elutriator after the removal of the $<10\mu$ fraction is allowed to settle in vessel L and is then run off into a weighed beaker keeping the volume of liquid as small as possible. The contents of the beaker are allowed to settle for a few minutes; the clean supernatant liquid is then poured off and the remainder evaporated to dryness on the steam bath and the residue weighed. The $>10\mu$ material is then re-dispersed in the same beaker and re-introduced into the elutriator, thus obviating any possibility of absorption of the smaller particles into the pores of the filter paper.'

'For separation of subsequent fractions, after removal of the $<10\mu$ material, the jet is changed for a larger size and the central fitting replaced. The water current is increased to that required to overflow particles approximately 20μ in diameter (4.2 ml. per second) and the overflow again filtered.'

'When elutriation has proceeded for one hour, the water current is stopped by turning on tap P and the sample is allowed to fall into the classifier L. Particles adhering to the upper classifier H are removed with a rubber policeman.'

'After half an hour the water current is re-started at the same velocity as before. The coarsest particles are now left behind in classifier L, which has an effective cross-sectional area approximately one-sixth of the upper, while elutriation proceeds in the upper classifier H as before. When elutriation of the fraction is completed, the elutriator is clipped at J and the tap P quickly turned. If method (2) has been adopted for dealing with the 10μ fraction, there will be no need to recover quantitatively the $10\text{--}20\mu$ fraction, providing the remaining fractions are weighed. It should, however, be dried and reserved for microscopical examination. The lower classifier L which contains the particles $>63\mu$ is also detached and its contents washed into a dried and weighed filter paper.'

'The apparatus is subsequently reassembled, tap K opened and the lower vessel L filled with water. The clip is removed, and the sample again allowed to fall into the lower classifier, after which the overflow is adjusted to 2.75 ml. per second and continued until the upper part of the lower classifier is clear, a process which usually takes less than two hours. The clip J is then replaced, the stop-cock P turned simultaneously and the material in L corresponding approximately to 0.05 mm. to 0.06 mm. transferred to a filter paper as before. The process of classification in the lower vessel L is repeated with overflows of 1.975 and 1.5 ml. per second, and finally the material remaining in the upper classifier H is also transferred to a filter paper. The graduated vessel M is employed when it is desired to note the volume of the fractions separated in vessel L.'

'The chart supplied by Messrs. International Combustion Ltd., with the Andrews instrument, is reproduced below:

		Upper Vessel			Lower Vessel		
Gauge Reading	Quantity <i>cc./sec.</i>	Velocity <i>mm./sec.</i>	Size <i>mm.</i>	Equiva- lent I.M.M. Mesh	Velocity <i>mm./sec.</i>	Size <i>mm.</i>	Equiva- lent I.M.M. Mesh
Medium Jet {	10.0	4.19	0.56	.021 600	3.5	.063	200
	8.5	3.75	0.50	.02 630			200
	4.5	2.75	0.37	.016 800	2.3	.051	250
	2.5	1.975	0.264	.013 1,000	1.65	.041	300
	Small Jet	4.0	1.50	0.20	.01 1,270	1.25	.034

In the course of extensive investigation in the author's laboratories with this elutriator, it has been found that, using the velocities given in the above chart at 20°C., and plotting the average particle size (measured microscopically) of the elutriated fractions against the average of the two velocities involved in their removal, the resultant curve is almost coincident with the theoretical curve representing Stoke's law. This applies both for quartz and for substances of higher density, providing the particles are approximately equidimensional thus confirming that in these circumstances the average particle sizes of elutriated fractions can be calculated from the density of the substance and the basic data for quartz.'

'The formula employed is:

$$d_s = D_s \sqrt{\frac{1.65}{D-1}}$$

where d_s = required average particle size.

D_s = corresponding average particle size for the siliceous filler for the velocities employed.

D = density of the substance elutriated.'

'Experiments at the same laboratories on the effect of temperature on elutriation indicated the desirability of controlling temperatures within at least $\pm 0.5^\circ\text{C}$., from which it follows that use of the elutriator at different periods of the year without any attempt at temperature control leads to serious errors.'

'The following modifications of the standard instrument have been found in the author's laboratories to increase its accuracy and also to enable temperatures to be more easily controlled: (1) The small constant head tank supplied is replaced by a considerably larger one; (2) the out-flow from the tank is attached to a copper coil immersed in a thermostatically controlled heating bath T and a thermometer

(R) enables the temperature of the water to be easily ascertained. Alternatively, the heating coil is interposed between the constant level tank and the main water tap, air bubbles evolved from the water thus being eliminated more easily.'

'It is advantageous to make all rubber connections as short as possible and to renew them frequently. Before use the apparatus should be thoroughly cleaned from grease with chromic acid; otherwise difficulties may be experienced through particles adhering to the glass. A further precaution is to ensure that the parts of the apparatus are vertical before commencing an experiment.'

Crook's Elutriator. This relatively simple apparatus was devised by T. Crook many years ago¹ and it is still to be seen operating in some laboratories, especially for instruction purposes. The general set-up is shown in Fig. 11A, and operation of this instrument is fully described by P. G. H. Boswell² and A. Holmes³. This apparatus obtains reasonable separations of sand, silt and clay grades (1 mm.-0.1 mm., 0.1 mm.-0.01 mm., and < 0.01 mm. particle-diameter respectively)⁴ for all practical purposes, but it is important that dimensions of the two cylindrical glass vessels A and B (Fig. 11A) should be strictly adhered to.

The following is the specification:

¹ Appendix to F. H. Hatch and R. H. Rastall, *Sedimentary Rocks*, (George Allen and Unwin, London), 1913, p. 349.

² *Memoir on British Resources of Sands and Rocks used in Glass-Making*, 2nd ed., (Longmans, Green, London), 1918, pp. 20-23.

³ *Petrographic Methods and Calculations*, (Murby, London), 1921, p. 209 and Fig. 40.

⁴ See particle-size classification, this chapter, p. 179.

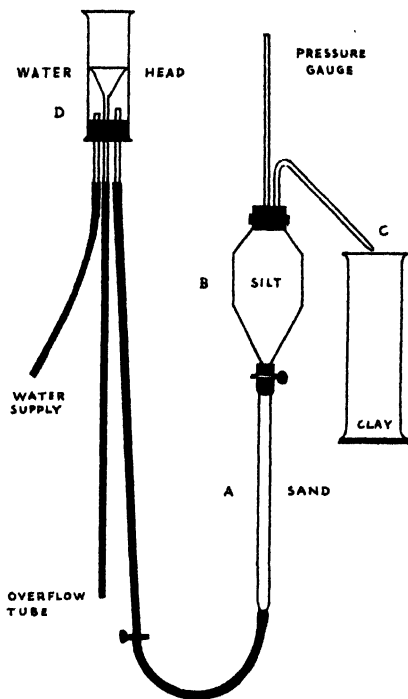


FIG. 11A. Crook's Elutriator (after A. Holmes). For separating sand, silt and clay.

- A. Lower sand tube, length not less than 30 cm., diameter 1.4 cm.
- B. Upper silt retainer, length about 30 cm., diameter 9 cm.
- C. Orifice, for clay residue, about 1 mm. diameter.
- D. Water-head, about 25 cm.

Velocity, 0.15 mm./sec. in A, 7.00 mm./sec. in B.

Rate of flow through apparatus, 1.08 cc./sec., or 100 cc. in 92 secs.¹

P. G. H. Boswell gives velocities of water-currents required for separating suitable grade-sizes with this type of apparatus as follows²:

<i>Diameter</i> (mm.)	<i>Velocity</i> (mm./sec.)
0.4	47
0.3	32
0.25	25
0.2	20
0.1	6.7
0.05	1.78
0.01	0.12

(Temperature 15°C.)

Some criticism of the Crook elutriator was made by H. A. Baker³ and is worthy of note for those using this apparatus:

- (a) Flow of liquid through A does not give uniform distribution of current over the cross-section.
- (b) Tube-wall exerts appreciable retarding effect; consequently velocity of current along central axis of A may approach twice that of calculated average.
- (c) Thus, some fine sand-grade will appear in B so that final percentage of sand calculated will be too low, silt too high.

It is pointed out that this error can be corrected by passing the dried silt product from B through a 0.1 mm. sieve and adding the residue on this sieve to the sand from A or to the fine sand screened from it⁴.

Single Vessel Elutriator. This type is in common use and it is generally agreed that more accurate results are obtained with it than with the original Crook's design above described⁵. The apparatus is shown in Fig. 11B and essential components are:

- A. Constant head vessel
- B. Elutriator
- C. Manometer
- D. Jet
- E. Collecting jar

¹ A. Holmes, *op. cit.*, p. 208.

³ *Geol. Mag.*, 1920, pp. 411 and 463.

⁵ P. G. H. Boswell, *op. cit.*, p. 25.

A. Holmes, *op. cit.*, pp. 213-215.

² *Op. cit.*, p. 20.

⁴ A. Holmes, *op. cit.*, p. 213.

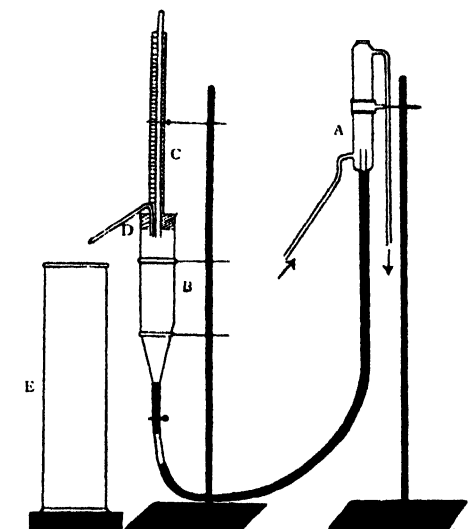


FIG. 11B. Single-Vessel Elutriator.

A—Constant head apparatus, B—Elutriator,
C—Manometer, D—Jet, E—Collecting jar.

Elutriator tubes may either be 51 mm. (2 in.) or 76 mm. (3 in.). Jet-aperture (D) may be varied in diameter to correspond with head of water and outflow per second through the jet. The data are summarized below¹:

Diameters (mm.) of			Head of Water (mm.)
Cylinder	Largest Grains Separated	Jet Aperture	
51	0.40	7	1,880
do.	0.20	3	1,400
76	0.10	3	700
do.	0.05	2	400

Procedure may be summarized as follows. The sample is dispersed in a suitable deflocculant (*e.g.* solutions of sodium carbonate, ammonia, sodium silicate or soap) and then transferred

¹ A. Holmes, *op. cit.*, p. 214.

by washing into elutriator B. Velocity of water is adjusted by means of constant head vessel A and size of jet D. The overflow product is collected in jar E, allowed to stand; the liquid is then decanted and the residue dried and weighed¹. For further operational data, reference should be made to the undermentioned authors^{2,3}.

Stadler Modification of Schoene Elutriator. This is a type of apparatus that has rather 'dated' and it is not often quoted in the literature these days; but it is certainly worthy of mention, especially for comparison with, for example, the Crook pattern. Advantages are that separation of grades between any desired particle-sizes can be made, up to eight or nine if required; *i.e.* estimation of *intermediate* grades (> 0.01 and < 0.05 , > 0.05 and < 0.1 mm., etc.) is possible by this means⁴. Disadvantages are that grade-sizes are separated one by one; operations must be closely watched; for a complete mechanical analysis the time-factor may be prolonged. The Stadler modification of the original Schoene model was to some extent inspired by the need, at the time, for some more or less straightforward method of classifying mineral-pulps from battery plant by mining-engineers⁵. The assembly is shown in Fig. 12, and identification of components is given below⁶.

- A. Elutriating cylinder
- B. Intake funnel for sediment
- C. Outlet tube
- D. Piezometer
- E. Variable jet
- F. Tank to provide fixed head of water
- G. Connecting tube for water-supply
- H. Screw-tap

For full details of construction and operation, the reader is referred to references^{5,6} below.

SEDIMENTATION

As will have been gathered from the section in this chapter on elutriation (p. 135), there is a practical lower limit to the latter process for classifying particles, *i.e.* about 10μ in diameter. Below

¹ *Note:* Preliminary calibration of this apparatus is advised before use. Measure the velocity of water at temperature of operation required to overflow particles of known size and density.

² A. Holmes, *op. cit.*, p. 214.

³ P. G. H. Boswell, *op. cit.*, pp. 25–26.

⁴ P. G. H. Boswell, *op. cit.*, pp. 23–25.

⁵ H. Stadler, Grading Analyses by Elutriation, *Trans. Inst. Min. and Met.*, 1912–13, p. 686.

T. Crook, *Roy. Dublin. Soc., Econ. Proc.*, 1, 1904, p. 267.

⁶ P. G. H. Boswell, *loc. cit.*

this size, sedimentation processes more than hold their own and measurements down to 0.2μ (less in certain cases) can now be comfortably made with modern apparatus and technique with considerable accuracy. Generally speaking, sedimentation procedures must be classed as indirect, *i.e.* actual separation of particles into different sized groups is not practicable. Size-distribution is assessed by measuring falling particles at a fixed level in a suspension and at successive intervals of time, either by weight or hydrostatic pressure; or other means may be employed for the same purpose, *e.g.* photoelectric sedimentometers (p. 157).

Literature on this subject, as with the manifold and varied problems of dispersion and suspension so intimately involved in sedimentation research, is nowadays enormous. It follows that within the space at our disposal here, only quite inadequate treatment is possible. It is hoped, however, that the selected references attached to the more important techniques herein described, will suffice to put the reader on to the right track to discover fuller knowledge of the particular processes with which he may be concerned in this fascinating field of petrographic analysis.

The general principle underlying sedimentation is embodied in the all-important Stoke's law, already discussed for purposes of elutriation (p. 135), but losing nothing by repetition here. This postulates that rate of fall (U) of a spherical particle bears direct relationship to its diameter (d); this function is expressed by the same equation previously quoted, *viz.*:

$$d = \sqrt{\frac{18\eta U}{(\rho - \rho')g}}$$

where g is acceleration due to gravity, ρ is density of the spherical particle, ρ' is density of the fluid medium and η is viscosity of

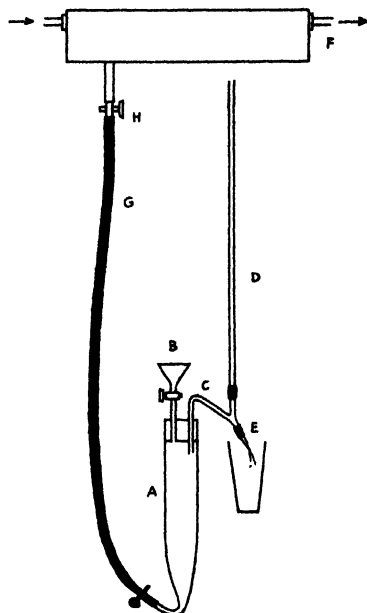


FIG. 12. Stadler's Modification of the Schoene Elutriator (after P. G. H. Boswell).

that medium. As in the case of elutriation, this equation constitutes the basis for calculating particle-size distribution from results of sedimentation processes. Caution in such calculations is advised for reasons due to certain limitations in application of this equation; this phase of the subject is well clarified by R. D. Cadle¹.

The fundamental difficulty in sedimentation analysis is usually the first step, adequate dispersion. If this is not attained, whatever follows afterwards is almost certainly doomed to failure. Recommendations as to how best to ensure complete dispersion of fine sediments are legion. But in the long run, in the author's experience, adequate dispersion depends by and large on trial and error with the particular material under investigation. Some traditional approaches to this problem are:

(a) *Boiling*. Sometimes successful for particles around 10μ , but seldom so for anything much finer. Some investigators criticize this method whatever the particle size².

(b) *Mechanical Dispersion*. Methods involving soaking in water and stirring³; strong agitation with water^{4,5}; breaking down in water in a mortar with rubber pestle or rubbing with a stiff brush⁶; these, individually or in combination, have proved quite efficient for the purpose in the instances cited.

(c) *Chemical Dispersion*. Addition of an electrolyte to water used in dispersion and suspension operations should prove helpful, providing no chemical reaction is involved with the material concerned. Well-tried examples are: dilute sodium carbonate; sodium oxalate⁷; sodium pyrophosphate; calcium chloride; potassium citrate; gum arabic (although not an electrolyte) is also useful in this connexion. Amount of electrolyte required is usually not more than 0.1 mol./litre. Wetting agents (colloidal electrolytes) have also been introduced with advantage in some difficult cases.

A somewhat novel method of dispersion, coming more or less within the same category, was put forward by W. C. Krumbein⁸ some years ago for unconsolidated sediments. It consists in shaking

¹ *Op. cit.*, p. 198.

² F. V. von Hahn, *Dispersoidanalyse*, (Steinkopff, Dresden), 1927, p. 272.

³ W. W. Rubey, *Lithologic Studies of Fine Grained Upper Cretaceous Sedimentary Rocks of the Black Hills Region*, U.S. Geol. Surv., *Prof. Paper 165a*, 1930, p. 1.

⁴ A. F. Joseph and O. W. Snow, *The Dispersion and Mechanical Analysis of Heavy Alkaline Soils*, *Journ. Agric. Sci.*, **19**, 1929, p. 106.

⁵ L. B. Olmstead, L. T. Alexander and H. E. Middleton, *A Pipette Method of Mechanical Analysis of Soils based on Improved Dispersion Procedure*, U.S. Dept. Agric., *Tech. Bull.*, **170**, 1930.

⁶ D. J. Hissink, *Die Methode der mechanischen Bodenanalyse*, *Inst. Mitt. für Bodenkunde*, **11**, 1921, p. 1.

⁷ L. B. Olmstead and *ors.*, *op. cit.*

⁸ *Journ. Sed. Pet.*, **2**, 1932, p. 44.

the sample with dilute sodium carbonate, removing $> \frac{1}{18}$ mm. mineral matter by wet sieving and diluting the $< \frac{1}{18}$ mm. fluid to 1 litre. An original weight of the sample is chosen such as to give 2–3 % suspension. The $> \frac{1}{18}$ mm. fraction is dried and weighed and the difference between this and the weight of original sample taken (air dried) gives the weight of fines in suspension. A check on the suspension is made by microscopical examination for presence of aggregates or flocculates, these being revealed by 'clusters' or 'long chain' forms; if these occur, dispersion is not complete; alternatively flocculation has intervened; remedial measures must then be taken before making any sedimentation test.

A more drastic, but none the less effective, method in obstinate cases, is to heat the sample to around 100°C. and then plunge it into cold water; this can be extended to heating to redness temperature, e.g. some crushed shales and consolidated clays, causing spontaneous breakdown into individualized particles on immersion. But this kind of action should only be resorted to with caution, backed at the outset by a thorough petrological knowledge of essential mineral composition and structure of the rock concerned and probably, as important, by a shrewd suspicion of what will be the outcome of the experiment.

L. Cohen¹ has recently given a considerable lead in this problem of dispersion. He reiterates the warning that 'the preparation of a fully dispersed, non-flocculating suspension is the key operation in the successful use of all liquid sedimentation methods.' Writing further in connexion with choice of liquid to be used in a special type of sedimentation balance (p. 160) (incidentally applicable to other techniques in sedimentation analyses), he emphasizes that '(a). . . density and viscosity should be such that the powder falls out in a reasonable time. Too long a time is inconvenient and may lead to inaccuracies in the column, and too short a time reduces the accuracy of the calculation; (b) it must be possible to disperse the powder in it, with or without a dispersing agent; (c) there must be no chemical or physical action between the liquid and the powder.'

The following data are extracted from Table 1 in Cohen's paper, in which are listed sedimentation liquids and suitable dispersing agents²:

¹ A Sedimentation Balance for Particle Size Analysis, *Instrument Practice*, October, 1959.

² For other dispersing agents for various materials see A. H. M. Andreasen, *Staub*, 43, 1956, p. 5; G. D. Joglekar and B. R. Marathe, *Journ. Sci. Ind. Res.*, 17A, 1958, p. 197.

<i>Powder</i>	<i>Liquid</i>	<i>Powder</i>	<i>Liquid</i>
Alumina	4	Iron oxide*	4
Barium sulphate	4	Limestone	7
Calcium phosphate	2	Magnesium oxide	4
Carborundum	4	Pyrite	5
Cement	7	Quartz	5
Coal	1, 2, 9	Silica	4
Graphite	8	Soil	9

* *Non-magnetic.*

Key 1, Acetone; 2, Alcohol; 4, Calgon in distilled water; 5, Glycol in distilled water; 7, 'Span 20' in iso-octane; 8, 'Teepol' in distilled water; 9, 'Tween 20' in distilled water.

'Apart from the choice of medium and dispersing agent the physical process of preparing a homogeneous suspension is most important. A technique found to be successful is as follows: the sample is placed on a watch-glass and a few drops of the dispersing agent added. . . . The mixture is worked with a small camel-hair brush until a smooth paste of honey-like consistency is obtained which is then gradually diluted with the medium, the brushing continuing in the early stages. When a dispersion of the correct concentration has been obtained it is boiled under reduced pressure, to remove any possibility of air bubbles forming, and finally stirred vigorously with a rotating brush. The suspension is examined with a low-powered horizontal microscope to find out whether dispersion is complete or whether agglomeration is occurring'¹.

Two other useful papers, one describing dispersion methods suitable for different types of sediments², the other concerned with exhaustive treatment of clays³ for the same purpose, should be consulted.

Of long-standing and modern approaches to particle-size analysis by sedimentation, those outlined below have been selected as being internationally representative. Fundamentally, with the possible exception of photoelectric technique, all are essentially variations on a similar theme, *i.e.* measurement of differential rate of gravitational fall of particles of varying diameter in a liquid medium of known viscosity, to accord with the practical application of Stoke's law (p. 135) for spherical particles.

Cumulative Sedimentation. This is, perhaps, sedimentation in its most direct form, and from results obtained, particle-size distribution in any given sample may be deduced usually by graphical

¹ L. Cohen, *op. cit.*

² W. C. Krumbein and R. H. Bray, Dispersion of Fine-Grained Sediments for Mechanical Analysis, *Journ. Sed. Pet.*, 3, 1933, p. 121.

³ R. E. Grimm and P. F. Kerr, Application of Clay Mineral Technique to Illinois Clay and Shale, *Bull. Geol. Amer.*, 46, 1935, p. 1909.

methods, not quite so direct. Consider a uniform suspension of previously well-dispersed particles of a sand-sample immersed in water in a suitable graduated glass vessel. After a predetermined time-interval, total amount of fine sand, silt, etc., remaining in suspension *above*, or more commonly total amount of sand settled out *below* a certain marked level in the vessel, is measured, collected and weighed. In actual practice, these measurements are made at successive time-intervals from start of test. Having got both weights and times recorded, the next step is to graph them, total fraction sedimented as ordinates, against time as abscissa from which a weight/time curve may be plotted. From this or a series of curves, particle-size distribution may be deduced by different formulae, the simplest and most straightforward being that devised by S. Oden many years ago¹.

Interpretation by this method is that for each point on the weight/time curve the following formula applies:

$$W = w + t \frac{dW}{dt}$$

where W = total fraction sedimented, t = time, w = coarse particle fraction, whose settling time for distance h equals or is $< t$, h being the maximum height of the sample suspension. dW/dt = slope of tangent to weight/time curve and this function multiplied by t gives the weight of fines in the sample. Tangents are drawn to the weight/time curve at several points and are used for calculating w for every point on the curve. Amount of fines which have settled down together with coarse material throughout the height of the liquid (h) are calculated from Stoke's equation for each tangential point on the curve; thus finally a cumulative particle-size distribution curve may be drawn for the sample as a whole. Other methods of arriving at the weight/time curve from sedimentation results and interpreting them cumulatively, are perhaps more accurate, but on the whole more complicated².

'Cumulative methods are rarely adopted in modern practice, since the curve relating mean concentration and time of settlement must be differentiated graphically in order to obtain the size analysis curve of weight undersize against particle diameter'³.

¹ *Proc. Roy. Soc. Edinburgh*, 36, 1916, p. 219; also *Kolloid-Zeit.*, 18, 1916, p. 33.

² R. D. Cadle, *op. cit.*, pp. 204-208; R. A. Fisher and F. Yates, *Statistical Tables for Biological, Medical and Agricultural Research Workers*, 3rd ed. (Oliver and Boyd, Edinburgh), 1948; A. E. Jacobsen and W. F. Sullivan, *Ind. Eng. Chem., Anal. Ed.*, 19, 1947, p. 855.

³ H. Heywood, *The Scope of Particle Size Analysis and Standardization*, *Trans. Inst. Chem. Eng. Supp.*, 25, 1947, p. 16.

Decantation. This has been described by R. D. Cadle¹ as a '... very simple but effective method of determining particle size distribution . . .'. The principle involves splitting a sample in two, one portion containing all particles $>$, the other all $<$, a predetermined size. These fractions can be broken down still further according to size and each weighed; from results, a cumulative particle-size distribution curve can be drawn.

The apparatus consists of a graduated cylinder comprising the sedimentation flask. Decantation is carried out by capping the flask with a two-hole stopper, one holding a glass sampling tube inserted to near the bottom of the flask, the other, a short tube used as air-blower to discharge the supernatant liquid. Recommended size of the flask is 200 ml., clearance between sampling tube and bottom of flask 3 mm., diameter of sampling tube 2-3 mm. The method has been criticized by some authorities² as simple but slow, not recommended as a method of analysis. On the other hand, accuracy is stated to be of the order of $\pm 1\%$. For further information and operational details see reference³ below.

Hydrometer Method. This is a procedure favoured in particle-size analysis of soils, but it is not universally popular. It is a modification of the Pipette Method (p. 158), but in operation probably simpler even than that technique once apparatus, calibration of hydrometer, procedure, and methods of calculation of particle-size from readings, are organized. It has the advantage in being relatively inexpensive to set up and is adaptable both for field and laboratory use. Full details of apparatus, test-procedure and methods of calculation will be found in the references cited below⁴.

Briefly, the method consists in measuring the density of a suspension at varying time-intervals 'after commencement of settlement, by means of a hydrometer. Dimensions and design of suitable long- and short-stem instruments are given in the D.S.I.R. publication⁴. Levels at which densities are successively measured correspond to the depth of the centre of the bulb of the hydrometer

¹ *Op. cit.*, pp. 222-24.

² B. A. Jarrett and H. Heywood, *Brit. Journ. Appl. Phys., Supp.* 3, 1954, p. 21.

³ R. D. Cadle, *op. cit.*, pp. 222-24.

⁴ *Soil Mechanics for Road Engineers*, D.S.I.R. Road Research Laboratory, (H.M. Stationery Office, London), 1952, pp. 46 and 517.

C. F. Armstrong, *Soil Mechanics in Road Construction*, (Arnold, London), 1950, p. 53.

B.S.1377 : 1948, *Methods of Test for Soil Classification and Compaction*, p. 44 (includes nomographic chart).

P. L. Capper and W. F. Cassie, *The Mechanics of Engineering Soils*, (Spon, London), 1949, p. 42.

R. D. Cadle, *op. cit.*, p. 215.

used below surface of the liquid. Concentration (c) of sediment, *i.e.* solids in g./litre remaining in suspension and measured at the end of any given time interval, is given by this equation:

$$C = \frac{1,000\rho_s}{(\rho - \rho')}(\rho_s - \rho')$$

where ρ_s = density of suspension, ρ = density of material, ρ' = density of fluid; densities in g./cc. Cumulative percentage in suspension (Pc) is given by:

$$Pc = \frac{100C}{C_1}$$

where C_1 is initial concentration of suspension¹.

Particle-size corresponding to elapsed time t at every hydrometer reading, is usually obtained by means of a nomographic chart compiled from experimental data. Such a chart and its method of use, are fully illustrated and described in the D.S.I.R. and B.S. publications cited². Calibration of the hydrometer used is an essential preliminary to experimental work; also certain corrections to hydrometer readings may have to be made for (a) meniscus (difference between top of meniscus and level of liquid); (b) temperature, if operating above or below normal hydrometer calibration temperature of 20°C. (68°F.); (c) dispersing agent (if used), since addition of such an agent may raise the density of the liquid³.

Discussing the hydrometer method, H. Heywood states⁴: 'this simple procedure has the disadvantage that as the hydrometer bulb is large compared with the depth of immersion of the centre of buoyancy, the condition implied in the incremental method is not fulfilled. Also, particles may settle on the shoulder of the bulb during the process of sedimentation, and the alternative of removing the hydrometer and re-inserting after the requisite time interval disturbs the suspension. These difficulties have been overcome and the essential simplicity of the method retained by Berg⁵ who uses a number of "divers", namely, small hollow glass vessels of known density, which take equilibrium positions in the suspension according to the density gradient'.

Light or Photo Extinction Methods. The principle underlying apparatus involving this particular mode of carrying out particle-size analysis, is dependent on measurement of optical density of a suspension of sediment by means of a photo-electric cell. Thus,

¹ R. D. Cadle, *op. cit.*, pp. 215-17. ² *Op. cit.*, pp. 49 and 62 (B.S., p. 47).

³ P. L. Capper and W. F. Cassie, *op. cit.*, pp. 42-44.

⁴ *Trans. Inst. Chem. Eng., Supp.* 25, 1947, p. 16.

⁵ S. Berg, *Studies on Particle-Size Distribution, Ingeniørvideenskabelige Skrifter*, 1940, No. 2, Danish Academy of Technical Sciences.

intensity of a narrow, parallel beam of light traversing such suspension, is decreased to an extent governed by concentration of the particles concerned. There are many advantages in adopting this procedure, among which may be mentioned: (a) use of very dilute concentrations; (b) very small quantities of sediment are sufficient if bulk is not available; (c) no disturbance of the suspension is necessary due to periodic sampling; (d) rapidity of readings of optical density, which can be recorded continuously if desired, hence obviating tedious evaporation of sample to dryness and subsequent weighing as is necessary with ordinary sedimentation methods; (e) no need to know weight of sediment in suspension as basis of determination of particle-size analysis on a percentage weight basis; (f) decreased errors arising from any uncertainties in precise measurement of height of suspension in the sedimentation vessel, owing to the use of a narrow light-beam¹.

Disadvantages, however, are not insignificant; they are both theoretical and practical. In the former category are the facts that (a) there is apparently a lower limit to particle size when optical density may be assumed to be proportional to the surface-area of particles²; (b) optical properties of suspensions are sensitive to design of the optical system employed in the apparatus³; (c) '... the basic theory which must be applied when dealing with materials having a wide particle size distribution is complicated and is worked out only for relatively simple cases'⁴.

On the practical side, conversion of optical density readings to weight percentages, *i.e.* particle-size distributions in the samples, is a time-consuming job. It involves the use of what is known as the 'Lambert-Beer' equation (together with Stoke's law) and relevant calculations do, at first glance, appear somewhat formidable; but this matter is lucidly clarified by R. D. Cadle, to whose discussion the reader is referred for details⁵.

One version of the light-extinction apparatus is known internationally as the 'Turbidometer'. It was originally developed by L. A. Wagner⁶ and still constitutes a standard method of test for the fineness of Portland cement⁷; it is, however, of far wider application than to cement alone, and natural sediments, also synthetic powder-products are alike within its orbit.

¹ R. D. Cadle, *op. cit.*, pp. 218-22.

² H. Heywood, *Trans. Inst. Chem. Eng. Supp.* 25, 1947, p. 16.

³ H. E. Rose and H. B. Lloyd, On the Measurement of the Size Characteristics of Powders by Photo-extinction Methods, *Journ. Soc. Chem. Ind.*, 65, 1946, pp. 52 and 65.

⁴ R. D. Cadle, *op. cit.*, p. 219.

⁵ *Op. cit.*, p. 219. See also F. M. Lea, *op. cit.*, p. 320.

⁶ *Proc. Amer. Soc. Test. Mat.*, 33, 1933, p. 553.

⁷ *A.S.T.M.*, C115-42 (1952), p. 137.

'The Wagner turbidometer consists essentially of a source of light of constant intensity adjusted so that approximately parallel rays of light pass through a suspension of the cement to be tested and impinge upon the sensitive plate of a photoelectric cell. The current generated by the cell is measured with a microammeter and the indicated reading is a measure of the turbidity of the suspension. General considerations indicate that turbidity is in turn a measure of the surface area of the suspended sample of cement'¹. This apparatus is fully described in the A.S.T.M. specification quoted above.

Another useful piece of apparatus is the photosedimentometer developed by W. F. Carey and C. J. Stairmand². The principle on which this instrument operates is magnification by an optical system of falling particles in a dilute suspension and at the same time a photographic record is made of the passage of the particles during exposure of predetermined duration. Particle-size is calculated from linear measurements of the paths photographed during the sedimentation cycle. H. Heywood comments³: 'the advantage is that a definite value of the equivalent Stoke's diameter is obtained from each particle observed but the disadvantage is the same as for the method of microscopical measurement, namely, that it is necessary to measure a very large number of tracks in order to obtain representative sampling over a wide range of particle sizes'.

The Heywood Photoelectric Sedimentometer is a new instrument for measuring particle size and particle size distribution in the sub-sieve range⁴. It provides a rapid method of particle-size measurement without necessity of preliminary sampling and weighing. It is claimed for this instrument that: 'it can be rendered almost automatic in operation and consists, in general, of the measurement by a photosensitive cell and microammeter of the light transmitted through a glass cell containing the sample to be tested when compared with a blank reference cell. From the formulae provided the specific surface may be calculated, and also the distribution of particle size.

'The photoelectric sedimentometer has successfully been used to determine the optical specific surface and particle size distribution of many materials in powdered form such as ground silica powders

¹ *A.S.T.M.*, loc. cit., p. 136. Note: For 'cement' quoted in this paragraph, substitute any other substance to which the method is potentially applicable.

² Size Analysis by Photographic Sedimentation, *Trans. Inst. Chem. Eng.*, **16**, 1938, p. 57.

³ *Trans. Inst. Chem. Eng., Supp.* **25**, 1947, p. 16.

⁴ *Brit. Pat.* No. 552398. Marketed by Griffin and George Ltd., Wembley, Middlesex; see catalogue of Chemical Laboratory Apparatus, **56S**, 1956, pp. 498-99.

and similar minerals, clays and silts, coal and coke dusts, activated carbons, graphite, pigments, metal powders, e.g. copper, tin and tungsten. The apparatus may also be used for colorimetric determinations¹.

Pipette Method. To most who have worked in the field of sedimentation research, the term 'pipette' has become almost synonymous with the name *Andreasen*², whose particle-size apparatus is so familiar in countless laboratories where sedimentation technique constitutes either a special problem or a day-to-day routine check on size-analysis of finely divided materials.

There are on the market in this country two varieties of the *Andreasen Particle Size Determination Apparatus*³. One comprises a 500 ml. cylinder graduated 0–20 cm. in 1 cm., and a 10 ml. pipette incorporating a double-bored stopcock with the stem of the pipette reaching down as far as the zero graduation on the cylinder. The other is designed so that samples from the suspension may be taken from any desired depth from surface. In this pattern the sampling pipette is held in place in a vertical stand, steel or wood, provided with levelling feet and fitted with a central vertical slide with rack and pinion operated height-adjustment. The stand incorporates a scale to measure movement of the slide. By this means the pipette is lowered into and withdrawn from the sample in suspension at any required depth in the cylinder (usually 1000 ml. capacity) without disturbance of the sedimentation.

Procedure is basically the same in both cases. The sample to be tested is first shaken up with water or other liquid, ensuring complete dispersion and production of a homogeneous suspension. Then by operating the pipette, 10 ml. fractions of the suspension are withdrawn at measured time intervals, using the two-way stopcock, transferred to weighed dishes, evaporated to dryness and weighed. Since the time taken to fall through unit distance in the suspension is a function of its size, the particle-size distribution can be calculated from weights of residue and intervals of time recorded between each withdrawal of the pipette.

An actual example may be quoted. Using the variable sampling depth apparatus, make up a suspension of the sample, commonly 2–3 % concentration, to 1 litre and transfer to a 1,000 ml. graduated cylinder; shake well. Allow to stand for such time as is sufficient to

¹ Griffin and George Ltd., *loc. cit.*

² H. Heywood, Measurement of the Fineness of Powdered Materials, *Proc. Inst. Mech. Eng.*, 140, 1938 p. 257; also G. A. Loomis, Grain size of White-ware Clays as Determined by the *Andreasen Pipette*, *Journ. Amer. Ceram. Soc.*, 21, 1938, p. 393.

³ Gallenkamp Ltd., London, Publication No. 591, 1958, p. 11; and General Catalogue (section: Particle Size), 1960, p. 646.

permit settlement of particles $> 10\mu$ to 10 cm. (time calculated from Stoke's law). Insert the pipette with its tip precisely at 10 cm. level and withdraw 10 or 20 ml. of the suspension; evaporate to dryness and weigh. Next, shake the suspension again, allow to stand for such time until particles $> 5\mu$ have settled to 10 cm. level; repeat the whole process as may be desirable by increasing the time of settlement of the suspension; in this way, further subdivisions in size-distribution may be made.

In the following data, relationship between diameter of particle, distance settled and time (given a sample of quartz S.G. 2.65, distance settled 10 cm. in water, and temperature of operation $20^{\circ}\text{C}.$), is shown¹:

Diameter of Particle μ	Distance cm.	Time		
		hr.	min.	sec.
10	10	—	18	40
5	10	1	14	41
2	10	7	47	—
1	10	31	7	—
0.5	10	124	30	—
0.1	10	3,112	—	—

From the above data it will be readily seen that the time factor may not impede determinations down to 1μ particle-diameter, but after that, except in special circumstances, procedure becomes uneconomic.

The pipette method assumes throughout that particles are spherical and obey Stoke's law (p. 135). Results therefore imply radii of spheres of the same density as particles under analysis by this method and having the same settling velocities. For all practical purposes, however, and providing due precautions are taken having regard to different materials of different density, the validity of the pipette method is sustained, at least within the size-range 50μ – 0.2μ in diameter.

Variations in technique with the pipette method have been suggested by several authors; references below will be found helpful in this respect^{2,3,4,5,6}.

Sedimentation Balance. The original design of a balance to measure particle-size directly from material settling from suspension by

¹ See L. J. Chalk, *Sedimentary Petrography*, 3rd ed., 1940, p. 107.

² F. V. von Hahn, *Dispersoidanalyser*, (Steinkopff, Dresden), 1927, p. 272.

³ H. Gessner, *Die Schlämmanalyse*, 1931, p. 21.

⁴ R. D. Cadle, *op. cit.*, pp. 212–14.

⁵ M. L. Smith, in G. Herdan, *Small Particle Statistics*, (Elsevier, New York), 1953.

⁶ H. E. Schweyer, *Sedimentation Procedures for Determining Particle Size Distribution*, Florida University and Industrial Experimental Station, *Bull. Ser. 54*, June 1952.

means of a balance-pan immersed in that suspension, was due to S. Oden¹. Although he and others subsequently made various improvements in the technique involved, much research has continued to be prosecuted by different workers to perfect the apparatus, with a result that there are available today some extremely valuable non-recording and automatically recording precision instruments.

The British design is due to W. Bostock² and is fully described by L. Cohen³. It consists of a graduated glass sedimentation tube surrounded by a water-jacket for thermostatic control. The lower end of the tube is covered by a metal balance pan having a 0.5 mm. clearance between pan and tube and both the latter are immersed in a 'clear liquid tank'; the upper end of the tube is joined by flexible pipes controlled by spring clips to the bottom and top of the pre-mixing vessel (Fig. 13). The pan connects with a torsion wire carrying a long light pointer at the end of which is a graticule, whose image is projected on to a ground glass screen; the reading is a direct measure of the load on the pan. Whatever variations there may be in density of the material being tested and of the fluid forming the suspension, are taken care of by a sensitivity control bob.

The following is an extract from the operation procedure described by L. Cohen³. 'The balance pan is clamped in position over the end of the sedimentation tube and the clear liquid tank is filled to above the level of the pan with the liquid to be used as the medium in the sedimentation. The appropriate volume (about 225 ml.) of suspension is poured into the pre-mixing vessel, the inside surface of which is coated with a silicone liquid-repellant to ensure that a negligible amount of the sample is retained, and the stop-cock at the top of the vessel closed. As quickly as possible the two spring clips are opened and the suspension run into the sedimentation tube. As soon as all the suspension has been transferred the clips are closed and a stop-watch started.

'The balance pan is released and the first reading of the balance scale is taken at 15 seconds, then at 30 seconds and subsequently at times increasing by a factor of $\sqrt{2}$. . .

'The scale readings are directly proportional to the fractional weight of the solid in the suspension deposited on the pan. The reading corresponding to the total weight of solid is obtained by allowing the sedimentation to continue until the liquid is clear and a steady reading is obtained. . .

'It is essential that the temperature of the sedimenting suspension be kept as constant as possible. In a normal draught-free room the

¹ *Int. Mitt. f. Boden.*, 5, 1915, p. 257.

² *Journ. Sci. Instrum.*, 29, 1952, p. 209.

³ *Instrum. Practice*, 13, 1959, p. 1036. This instrument is also known as the 'Gallenkamp Sedimentation Balance' and is marketed by that firm in London.

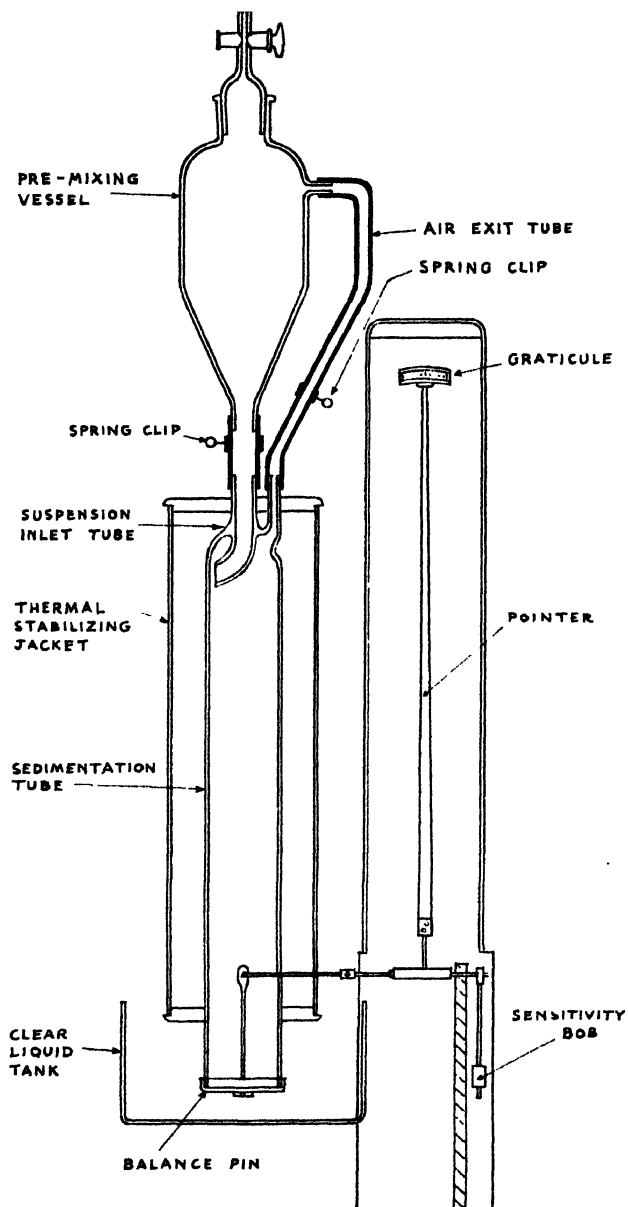


FIG. 13. Diagram of Sedimentation Balance

(Courtesy L. Cohen and Simon Carves Ltd., Stockport.)

water jacket is usually sufficient stabilization although it may be necessary to circulate water from a thermostat bath. A constant-temperature room is an advantage.¹

Calculations of results obtained with this apparatus are somewhat complicated, but certain 'short cuts' can be made and are described in the paper quoted¹.

Basic equation of the instrument is:

$$p = w + t \left(\frac{dp}{d(\ln t)} \right)$$

which, for purposes of computation, may be transposed thus:

$$w = p - \frac{dp}{d(\ln t)}$$

where w = fraction (by weight) of particles $>$ a diameter d , calculated by Stoke's law, from height of suspension above balance pan (h cm.), density of solid (σ g./ml.), density of liquid (ρ g./ml.) and viscosity of liquid (η poise).

The relation is thus:

$$d^2 = \frac{18h\eta}{(\sigma - \rho)tg} \times 10^8$$

where t = time (secs.), g = acceleration due to gravity (cm./sec.²).

'In other words, in a given test there corresponds to any time t a particle diameter d .

'The experimental results are plotted in the form: fractional weight deposited (p) against natural logarithm of time ($\ln t$) . . . and $dp/d(\ln t)$ obtained by graphical differentiation of the curve at appropriate values of t ².

It is claimed for this sedimentation balance that particle-size distribution within the range 5–75 μ is practicable, but if the 'over-size' is not $> 20\mu$ (approx.), the lower limit of the range is about 2 μ . Diverse materials can be mechanically analysed with this instrument, *e.g.* alumina, carborundum, china clay, cement, felspar, flint-flour, limestone, pyrite, plastics, etc.; also dusts deposited by electrostatic precipitators, cyclones from boilers, blast-furnace and flash-roaster plants.

'The present trend in instrument design is toward automatic recording wherever possible and in keeping with this trend an automatic recorder for the Sedimentation Balance is under development. Briefly, the device makes a photographic record of the balance reading at the selected time intervals (approximate multiples of $\sqrt{2}$) so that once the test is started no further attention is

¹ L. Cohen, *loc. cit.*, 1959.

² L. Cohen, *loc. cit.*, 1959.

required until the test is complete. This means that a number of balances could be used by one operative and, in fact, tests could be left on overnight. It is hoped that this recording attachment will be available commercially in the near future¹. (Pl. 2).

Automation in technique of particle-size determination has been achieved in at least one extremely ingenious, but somewhat complex and expensive model, namely the Sartorius Sedimentation Balance². This balance was developed in co-operation with Dr. Bachman and 'records the increase in weight of a sediment deposited on the pan as a function of time. In this way the grain size distribution curve of the sediment can be deduced from the curve obtained. Particle sizes between 1 and 60 microns, which are usually outside the range of a screen analysis, can be determined by this method'².

A summary of operational details with this apparatus may be quoted, which gives an idea of comparative simplicity in use, apart from complexity of design:

'The weight of the sediment deposited on the pan in the sedimentation vessel changes the normal position of the balance beam which movement allows a spot of light to be directed on a photo-cell. At a fixed light intensity the photo-cell operates a step-by-step motor. This motor twists a torsion wire to a pre-set angle. The elastic force transmits a torsional moment to a small beam fixed to the torsion wire which in turn is transmitted to the main balance beam by a mechanical coupling turning it back to its balanced position. In this way the moment developed by the load on the pans is automatically compensated. This procedure is repeated until the suspended particles are completely settled. At the same time, the recording pen will be moved 0.08 cm. over the paper at each switching action of the motor. The paper moves at a constant speed at right angles to the pen movement and a stepped curve is obtained representing the weight on the pan as a function of time³.'

The limitations of Stoke's law have been applied for the test conditions implicit with this instrument and final calculations are similar to the Gallenkamp non-recording apparatus (p. 160).

Mention is made by L. Cohen⁴ of the Shirnadzu Sedimentograph, also a recording instrument for automatic particle-size determination. The significant reference to this apparatus is quoted below⁵.

¹ L. Cohen, *loc. cit.* 1959. Note: The Gallenkamp Sedimentation Balance Recording Attachment is now on the market. (Pl. 2).

² Manufactured by Sartorius-Werke A G, Göttingen; marketed in the United Kingdom by Hudes Merchandising Corporation, Ltd., London, W.1. See pamphlet in English and working booklet for this instrument (in German) giving full details of applications and calculations.

³ Pamphlet in English: see ref. ².

⁴ *Loc. cit.*, 1959.

⁵ E. Suito and M. Arakawa, *Bull. Inst. Chem. Res., Kyoto University*, 22, 1950, p. 7.

For further information on non-recording sedimentation balances, see refs.^{1,2} below.

SIEVE ANALYSIS

This time-honoured practice of ascertaining particle-size distribution of incoherent materials, is unquestionably the most universally liked method today, within the confines of certain restrictions. It is only when the lower practical limit to sieving is reached (around 50μ), or when a much more accurate mechanical analysis of a sediment is sought, that appeal is made to the specialized techniques previously described in this chapter. A refreshingly apposite commentary on the subject was given by H. Heywood³ some years ago and it is still so true that it is well worth while repeating here, as a most fitting introduction to this present section:

"Sieving has been used for the grading of powdered materials since the days of antiquity, and may aptly be described as the "Cinderella" of sizing processes, for it does most of the hard work yet is greatly neglected as regards research. This attitude is regrettable, for with proper attention to detail and to standardization, sizing by means of sieves can be very accurate within the limits of its application. The accuracy of sieving analyses is limited by the necessary tolerances in the weaving of the sieve cloth, and by the effect of irregularity in particle shape. Fractionation by means of sieves is a function of two dimensions of the particle, these being the maximum breadth and maximum thickness; for unless the particles are excessively elongated the length does not hinder the passage of the particles through the sieve apertures. The dimensions and tolerances of sieve apertures are now standardized in different countries, but insufficient attention has been given to the method of sieving apart from applications to a specific material such as Portland cement. Sieving is a statistical process, that is, there is always an element of chance as to whether a particle will or will not pass the apertures, and hence there is no definite "end point" to sieving analysis. The "end point" must therefore be defined arbitrarily, either by a fixed time of sieving or by sieving until particles pass the sieve at a fixed rate per minute."

For present purposes it will suffice to describe sieve series commonly employed in English-speaking countries, together with one example representing European (continental) custom, as standardized in the German series, the equivalent of which in France is known as the 'Afnor' series.

¹ W. M. Dotts, *Ind. Eng. Chem. Anal. Ed.*, **18**, 1946, p. 326.

² K. Kammermeyer, *Ind. Eng. Chem. Anal. Ed.*, **13**, 1941, p. 335.

³ *Trans. Inst. Chem. Eng., Supp.* **25**, 1947, p. 15.

In the British range, there are the Institution of Mining and Metallurgy Standard Screens (I.M.M.) which appeared as long ago as 1907. There are also the now extensively employed British Standard series of coarse, medium, and fine-mesh sieves, first put forward by the British Standards Institution in 1931, and which have now largely superseded the I.M.M. sieves. In the United States the W. S. Tyler Company, Cleveland, Ohio, first marketed in 1910 a series of sieves which had previously been standardized by the U.S. Bureau of Standards. Then in 1919, the Bureau of Standards formulated a new series under title of the United States Standard Sieve Series, which was ultimately adopted by the American Society for Testing Materials (A.S.T.M.) in 1926. The German Standard Sieve Series is known as DIN No. 1171 and is favoured by continental workers.

Institution of Mining and Metallurgy (I.M.M.) Series. Size-range 5–200, sieve numbers being 5, 8, 10, 12, 16, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 150, 200¹. The chief feature of I.M.M. screens is that aperture-size equals diameter of wire as woven, thus effective sieving area of all sizes is 25%. Aperture-sizes in this series are easily calculated, e.g. 200 mesh screen contains 200 apertures and 200 thicknesses of wire to the inch; the aperture is thus 1/400th in., or 0.0025 in. Disadvantages of the I.M.M. sieves are relatively small screening area and absence of any mathematical relationship between successive sieves in the series.

British Standard (B.S.) Sieves. (a) *Fine Mesh Test Sieves.* Size-range, 5–300 mesh, sieve numbers being 5, 6, 7, 8, 10, 12, 14, 16, 18, 22, 25, 30, 36, 44, 52, 60, 72, 85, 100, 120, 150, 170, 200, 240, 300. (b) *Medium Mesh Test Sieves.* Size-range $\frac{1}{32}$ in. – $\frac{1}{2}$ in. mesh, sieve numbers being $\frac{1}{32}$, $\frac{1}{16}$, $\frac{1}{8}$, $\frac{3}{16}$, $\frac{1}{4}$, $\frac{5}{16}$, $\frac{3}{8}$, $\frac{1}{2}$ in. (c) *Perforated Plate for Coarse Test Sieves.* Size range $\frac{3}{16}$ in. – 4 in., sieve numbers being $\frac{3}{16}$, $\frac{1}{4}$, $\frac{5}{16}$, $\frac{3}{8}$, $\frac{1}{2}$, $\frac{5}{8}$, $\frac{3}{4}$, $\frac{7}{8}$, 1, $1\frac{1}{8}$, $1\frac{1}{4}$, $1\frac{1}{2}$, $1\frac{3}{4}$, 2 , $2\frac{1}{4}$, $2\frac{1}{2}$, 3 , $3\frac{1}{2}$, 4 in.²

The chief features of B.S. fine mesh sieves are screening area varying from 35% to 44%; apertures of consecutive sieves are substantially $\sqrt{2} : 1$ ratio. Apertures in the medium series are not based on $\sqrt{2} : 1$, but successive increments are simple fractions of 1 inch. Screening area varies from 36% to 63%. Coarse mesh sieves have square apertures and square pitch with screening area varying from 53% to 64%.

*American Society for Testing Materials (A.S.T.M.) Series*³. The sieve designations are divided into two categories, fine and coarse. For the former, size-range is $3\frac{1}{2}$ –400 (fine mesh), sieve numbers being $3\frac{1}{2}$, 4, 5, 6, 7, 8, 10, 12, 14, 16, 18, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 100, 120, 140, 170, 200, 230, 270, 325, 400. For the coarse series, size-range is

¹ For equivalent apertures in mm., see table on p. 167.

² For equivalent apertures in mm., see table on p. 167. See also B.S.410 : 1943, Test Sieves, for full details of the series, construction, examination, measurement and calibration.

³ A.S.T.M. designation: E11–39.

$\frac{1}{4}$ -in.-4.24 in., sieve numbers being $\frac{1}{4}$, 0.265, $\frac{5}{16}$, $\frac{3}{8}$, $\frac{7}{16}$, $\frac{1}{2}$, 0.530, $\frac{5}{8}$, $\frac{3}{4}$, $\frac{7}{8}$, 1, 1.06, $1\frac{1}{4}$, $1\frac{1}{2}$, $1\frac{3}{4}$, 2, 2.12, $2\frac{1}{2}$, 3, $3\frac{1}{2}$, 4, 4.24 in. Apertures in the fine series are based on the $\sqrt[3]{2} : 1$ ratio, as with Tyler intermediate sieves (*q.v.*), the only difference being that the U.S. Standard Sieve Series employs a sieve of 1.00 mm. aperture as its basic standard.

Tyler Standard Screen Scale Series. Size range $2\frac{1}{2}$ -400 mesh, sieve numbers being $2\frac{1}{2}$, 3, $3\frac{1}{2}$, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 20, 24, 28, 32, 35, 42, 48, 60, 65, 80, 100, 115, 150, 170, 200, 250, 270, 325, 400 mesh. The Tyler screen scale 'has as its base an opening of 0.0029 in which is the opening in the standard 200-mesh testing sieve, the openings increasing or decreasing in the ratio of the square root of 2 or 1.414. Where closer sizing is required . . . with intermediate sieves . . . openings increase in the ratio of the fourth root of 2 or 1.189¹. In practice, the difference between the Tyler and the A.S.T.M. series is so small as to be negligible and sieves of the two series can be used interchangeably.

German Sieve Series. German Standard Specification DIN 1171: 1934. Size range: $3\frac{1}{2}$ -250 equivalent mesh A.S.T.M. DIN No. 1-100, *i.e.* 1-10,000 mesh/sq.cm. or 6,000-0.060 mm. apertures².

A comparison of apertures (mm.) and sieve mesh numbers of the I.M.M., Tyler, A.S.T.M., B.S. and German DIN series is made in the data on facing page. It will be noted that the following sieves have nearly identical apertures:

TYLER	A.S.T.M.	B.S.	DIN
200	200	200	280
170	170	170	170
150	140	150	160
100	100	100	140
80	80	85	—
60	60	60	24
48	50	52	20
35	40	36	14
28	30	25	10
20	20	18	—
14	16	16	6
9	10	8	3
6	6	5	2

Sieve-Frame Dimensions. Unless otherwise specified, in the B.S. series it is customary to employ 12 in. or 18 in. diameter cylindrical frames for perforated plate³ (coarse) test-sieves, and commonly

¹ R. D. Cadle, *op. cit.*, Table I, pp. 176-77. This gives an exhaustive description of this Screen Scale Series.

² See B.S.410 : 1943, Appendix D and R. D. Cadle, *op. cit.*, Table III, pp. 182-83.

³ B.S.410 : 1943, Pt. IV; also B.S.1669 : 1950, Industrial Perforated Plates.

Sieve No.	Aperture in mm.				
	I.M.M.	TYLER	A.S.T.M.	B.S.	DIN*
400	—	0.037	0.037	—	—
325	—	0.044	0.044	—	—
300	—	—	—	0.053	—
270	—	0.053	0.053	—	—
250	—	0.062	0.062	—	—
240	—	—	—	0.066	0.060 (100)
230	—	—	0.062	—	—
200	0.063	0.074	0.074	0.076	0.075 (80)
170	—	0.088	0.088	0.089	0.088 (70)
150	0.084	0.104	—	0.104	0.102 (60)
140	—	—	0.105	—	0.102 (60)
120	0.107	—	0.125	0.124	0.120 (50)
115	—	0.124	—	—	0.120 (50)
100	0.127	0.147	0.149	0.152	0.150 (40)
90	0.139	—	—	—	—
85	—	—	—	0.178	—
80	0.157	0.175	0.177	—	—
72	—	—	—	0.211	—
70	0.180	—	0.210	—	—
65	—	0.208	—	—	0.200 (30)
60	0.211	0.246	0.250	0.251	0.250 (24)
52	—	—	—	0.295	—
50	0.254	—	0.297	—	—
48	—	0.295	—	—	0.300 (20)
45	—	—	0.35	—	—
44	—	—	—	0.353	—
42	—	0.351	—	—	0.385 (16)
40	0.317	—	0.42	—	—
36	—	—	—	0.422	—
35	—	0.417	0.50	—	0.430 (14)
32	—	0.495	—	—	0.490 (12)
30	0.421	—	0.59	0.500	—
28	—	0.589	—	—	0.600 (10)†
25	—	—	0.71	0.599	—
24	—	0.701	—	—	—
22	—	—	—	0.699	—
20	0.635	0.833	0.84	—	—
18	—	—	1.00	0.853	—
16	0.792	0.991	1.19	1.003	1.020 (6)
14	—	1.168	1.41	1.204	1.200 (5)
12	1.056	1.397	1.68	1.405	—
10	1.270	1.651	2.00	1.676	1.500 (4)
9	—	1.981	—	—	2.000 (3)
8	1.574	2.362	2.38	2.057	2.400 (2½)
7	—	2.794	2.83	2.411	—
6	—	3.327	3.36	2.812	3.000 (2)
5	2.540	3.962	4.00	3.353	—
4	—	4.699	4.76	—	—
3½	—	5.613	—	—	6.000 (1)
3	—	6.680	—	—	—
2½	—	7.925	—	—	—

* Numbers in parentheses () refer to DIN sieve numbers.

† Sieve No. 11 has aperture 0.540 mm., no equivalent sieve number in the left-hand column.

8 in. (though occasionally 12 in.) diameter frames for fine and medium mesh sieves. Where mechanical sieving is in force, requirements are normally 8 in. diameter sieves (with corresponding lids and pans), which take care of 5 mesh–200 mesh in the B.S. series and similarly up to 200 mesh in U.S. series. It has, however, been found useful in much of our work to have a specially constructed 8 in. diameter $\frac{1}{8}$ in. mesh sieve to use in nesting in the mechanical shakers (standard size supplied in the same mesh for hand-sieving would normally be 12 in. diameter).

In the A.S.T.M. range, sieve frames for coarse particles having nominal openings < 1 in. may have standard 8 in. frames, larger if required, and may be square or circular. In sieve frames for sieves for fine series, standard frames are circular and 8 in. diameter, but 3 in. diameter sieves are permitted for 100 mesh and finer materials. With perforated plate sieves, having circular openings 1 in. in diameter or larger, frames larger than 8 in. in diameter are recommended.

Summarily, considered internationally, although 8 in. and 12 in. circular sieve-frames are conventional sizes for hand-operation over the whole range of available sieves, there is much latitude permitted in specification to suit individual requirements. It is only when mechanical shaking is involved that sieve-frame restriction to 8 in. diameter is automatically imposed for some laboratory types (see, however, p. 175).

Technique. As a rule sieve analysis of sediments is not carried out on material less than 50μ particle-size, at least by the dry method. The existence of 270, 300, 325 and 400 mesh sieves does of course imply a possible lower range of sizing, 53μ – 37μ , by this means, but their use is exceptional in routine work and even then wet sieving is nearly always inevitable. Normally, the lower limit is the 200 mesh sieve (75μ) and no difficulty should be experienced with this either dry or wet. For all practical purposes in the sub-sieve range, elutriation or sedimentation is the rational procedure.

Individual or casual sieving is commonly carried out by hand, but where routine analyses are involved mechanical shakers are much to be preferred, because they have the advantage of standardizing both method and time of shaking and thus are productive of more consistent results than hand sieving, combined with a degree of uniformity which greatly facilitates comparison of sieving results on the same material by different operators. It is therefore convenient to consider procedure under three main operational categories, (A) hand-sieving dry, (B) hand-sieving wet, and (C) mechanical shaking.

(A) *Hand-sieving, Dry.* To illustrate the technique, consider the mechanical analysis of a sample of natural gravel containing 1-in. nominal size pebbles down to fines (for petrological classification of known particle-sizes into gravel, sand, silt and clay, see relevant section in this chapter, p. 178). The procedure outlined is that consistently adopted for such a sediment in the author's laboratories over many years past; it has proved to be both accurate and efficient. (Mechanical shaking is excluded from discussion at this stage, but that technique often comprises a realistic combination of this and hand-sieving.) Operations are as follows:

(i) Providing the amount of 1-in. material is not excessive¹, at least a 5-kg. bulk-sample (to be truly representative of the mass, preferably after quartering down² from a much larger bulk, say minimum 56 lb. in this case) is taken; this amount (5 kg.) is first dried if necessary, then weighed.

(ii) The sample is next placed on, say, the $\frac{3}{16}$ mesh B.S. sieve and shaken until nothing more passes that screen; this effectively splits the sample on a dividing line of $\approx \frac{3}{16}$. The range of sieves selected in this example for the whole operation is 2, $1\frac{1}{2}$, 1, $\frac{3}{4}$, $\frac{1}{2}$, $\frac{3}{8}$, $\frac{1}{4}$, $\frac{3}{16}$, $\frac{1}{8}$ inch (coarse portion), 7, 14, 25, 52, and 100 mesh (fine portion). Sizing of the coarse fractions is carried out separately on single sieves, a time-consuming operation, but necessary where a high degree of accuracy is the aim. The process is repeated until all the $> \frac{3}{16}$ fractions have been isolated.

(iii) Next, a representative portion of the $< \frac{3}{16}$ in. material is placed on the $\frac{1}{8}$ mesh sieve and shaken, and so on in succession until ultimately the finest (in this case < 100 mesh) fraction is isolated.

(iv) Each sieve fraction is weighed once the operator is satisfied that it represents as complete a segregation as is possible.

(v) The weight of each fraction is expressed as percentage of the original sample, with summation to 100. The results of this particular example between sieves are as follows:

<i>B.S. Sieve</i>	<i>Sample</i>
Retained on 2 in.	Nil
$1\frac{1}{2}$ in.—2 in.	1.0
1 in.— $1\frac{1}{2}$ in.	5.8
$\frac{3}{4}$ in.—1 in.	4.0
$\frac{1}{2}$ in.— $\frac{3}{4}$ in.	7.3
$\frac{3}{8}$ in.— $\frac{1}{2}$ in.	6.0
$\frac{1}{4}$ in.— $\frac{3}{8}$ in.	7.8
$\frac{3}{16}$ in.— $\frac{1}{4}$ in.	5.1
$\frac{1}{8}$ in.— $\frac{3}{16}$ in.	3.9
7 mesh— $\frac{1}{8}$ in.	3.3

See table on p. 171.

² See Ch. II, p. 71.

(Contd. on p. 170)

(Contd. from p. 169)

<i>B.S. Sieve</i>	<i>Sample</i>
14-7 mesh B.S. sieve	6.5
25-14 mesh B.S. sieve	8.9
52-25 mesh B.S. sieve	20.0
100-52 mesh B.S. sieve	16.7
Passing 100 mesh B.S. sieve	3.7
Total	100.0

Or the results may be expressed as cumulative percentage passing B.S. sieves as follows:

<i>B.S. Sieve</i>	<i>Sample</i>
2 in.	100.0
1½ in.	99.0
1 in.	93.2
¾ in.	89.2
½ in.	81.9
⅜ in.	75.9
¼ in.	68.1
⅜ in.	63.0
⅛ in.	59.1
7 mesh	55.8
14 mesh	49.3
25 mesh	40.4
52 mesh	20.4
100 mesh	3.7

It is often quite unnecessary to indulge in so many sieves as in the foregoing example. For instance, it may be simply a case of isolating a definite particle-size from a sample, when two limiting sieves will suffice; or, if a general idea of particle-size distribution is aimed at, probably five or six carefully-selected sieves will satisfy the problem.

Equally, experience alone can influence the decision as to what minimum weight of a given sample of aggregate will, by sieving, give a reasonably accurate picture of its inherent particle-size distribution. Much depends on a critical scrutiny of the sample as first received, and on the maximum size particles present in substantial proportion.

As a guide, the following data quoted from B.S.812 : 1951 will be found useful¹:

¹B.S.812 : 1951, Part III, Table 5, p. 18. (Revised 1960). (Reproduced by permission of the British Standards Institution.)

Maximum size of material present in substantial proportion	Minimum weight of sample to be taken for sieving	
<i>in.</i>	<i>kg.</i>	<i>lb.</i>
2½	50	110·231
1½	25	55·116
1	10	22·046
¾	5	11·023
½	2·5	5·511
⅜	1	2·204
¼	0·500	1·102
⅛	0·250	0·551
Passing		
No. 7 mesh	0·100	0·220
No. 200 mesh	0·010	0·022

The above data on sample sizes normally provide adequate and representative samples of aggregate without overloading, a hazard to be avoided for many reasons. B.S. 812 : 1951 again is helpful in this connexion and the following table gives an idea of the maximum desirable weight of material to be retained on each sieve at completion of sieving¹:

B.S. Sieve	Maximum Weight	
<i>in.</i>	<i>kg.</i>	<i>lb.</i>
1½ or over	5	11·023
1	4	8·818
¾	3	6·613
½	2	4·409
¾ or ½	0·500	1·102
¾ or ½	0·400	0·881
No. 7	0·200	0·440
No. 10 or 14	0·100	0·220
No. 18, 25 or 36	0·075	0·165
No. 52 or 72	0·050	0·110
No. 100	0·040	0·088
No. 200	0·025	0·055

Here are some practical 'tips' to aid the beginner in the art of sieving (it is really a highly skilled job; proficiency is won only by experience)²:

¹ Table 6, p. 20. (Reproduced by permission of the British Standards Institution.)

² See particularly B.S.1796 : 1952, Methods for the Use of B.S. Fine-Mesh Test Sieves, clauses 2, 4, 6, 7; also B.S.812 : 1951, Part III, pp. 18-21. (Revised 1960).

- (a) Movement of sieving by hand consists in swirling the particles round the sieve by circular motion clockwise, then anticlockwise, at the same time giving the sieve a slight vertical bias: a combination of lateral rotation and up-and-down disturbance. *The secret of success is to keep the particles continually on the move and in frequently changing directions.*
- (b) A sieve may be tapped tangentially by hand to ease passage of particles, but it should *never* be banged on the bench
- (c) Cover and bottom to sieves may be dispensed with where speed is paramount or other consideration warrants, when sieving over a clean sheet of white or black glazed paper may be resorted to.
- (d) If aggregates or agglomerations of particles are present, it is permissible to crush them gently with the fingers against the wall, but *never against the woven mesh* of the sieve.
- (e) Use of a free-moving coin in the powder to facilitate passage of competent particles through the mesh, favoured by some operators, is of doubtful value and to be deprecated.
- (f) Use of stiff brushes or any hand-manoeuvred implement to exert pressure on particles in their passage through sieve apertures, is in the author's opinion highly undesirable, '... but resort may be made to this procedure with certain materials which are particularly difficult to sieve¹'. Light brushing with a fine camel-hair brush both on surface of and on underside of sieves, is permissible on the 100 and finer mesh sieves².
- (g) In the case of unusually dirty samples, e.g. clay-coated pebbles or particles, it may be necessary to wash coarse and fine portions before sieving. This adds considerably to the time-factor for the whole operation. Whatever is washed off must be recovered by evaporating to dryness, weighing, sieving separately and adding residues to the appropriate master-fractions, a tedious process which may, however, be shortened in certain circumstances by wet-sieving throughout.
- (h) As regards time, sieving is generally considered to be complete when not more than 0.05% by weight of material passes through the sieve after agitation for one minute. Procedure by hand-sieving to the 'end point' by the rate-test is described in B.S. 1796³. As a result of considerable experimentation on the effect of time and load on efficiency of sieving sand, F. A. Shergold⁴ arrived at the conclusion that if screens are not overloaded, i.e. if sample loads are between about 40 and 150 g., then maximum sieving time is around 9 minutes. With the 200 mesh sieve, time for complete separation is often much longer, up to 30 minutes or more.
- (i) Keep all sieves scrupulously clean, especially the fine mesh units, and in good repair. Well-fitting sieves are a *sine qua non* to accurate

¹ B.S.1796 : 1952, p. 6.

² B.S.812 : 1951, Part III, p. 19. (Revised 1960).

³ *Op. cit.*, clause 7.

⁴ *Journ. Soc. Chem. Ind.*, 65, 1946, p. 245

work. Keep them so. When they are worn and become loose-fits, they are not only difficult to repair, but are unsuitable for accurate work. They should then be scrapped. Holes in the gauze can be soldered, but not indefinitely; such remedial measures if excessive, restrict screening space and decrease efficiency. Better, in the interests of accuracy, to purchase a new set.

(B) *Hand-sieving, Wet.* Wet sieving finds its chief exponents in those who perforce have to manipulate sediments prone to form aggregates, either naturally or because of shaking; sediments already suspended in liquids, and in the fine size-range of 200–400 mesh. Liquids concerned are usually water, but industrial methylated spirit or white spirit is employed where the material is likely to be reactive with water. It is generally conceded that wet sieving increases the total amount of material passing through a given sieve, especially in the finer size-range, compared with corresponding dry sieving.

Wet sieving is best confined to individual sieves, each constituting a separate operation, but, with caution, it can occasionally be extended to a small nest of sieves. The procedure is normally to run a suspension of the sediment through the sieve(s) with copious supply of water (or other liquid) to hand. In cases where much routine wet-sieving of fine powders is involved, special sieves with deep frames are available, to avoid overspill of sediment during washing.

The sequence in sieving wet is very much the same as under dry conditions, if a series of sieves is concerned; begin at the coarsest size and work downwards. A good idea of what is involved with finest materials, is formed from the method of preliminary removal of fine dust from a sample as described in B.S.1796 : 1952¹. 'Very fine particles are more quickly eliminated by wet sieving than by any other method, and indeed this is often the only successful method of treatment for fine powders with only a small percentage residue on the sieve, e.g. pigment materials. Wet sieving may reduce the breakage of some friable or fragile materials; it will also disperse aggregates and may give different results from those obtained by dry sieving'².

Some pertinent 'tips' on the subject of wet sieving may be added:

- (a) The very nature of an aqueous process obviously means that sieves must be thoroughly dry both before and after use. For this purpose, a thermostatically controlled oven is valuable, with shelves both in area and number to accommodate sieves in a horizontal position. Alternatively, a hot plate may be used; or the more modern and refined infra-red radiation drier.

¹ Clause 6, p. 9.

² B.S.1796 : 1952, clause 2, p. 6.

- (b) When drying sieves, always avoid high temperatures and possibility of overheating.
- (c) Sieves, when drying, should never be in contact directly with actual source of heat.
- (d) Examine periodically sieve-frame seams used for wet sieving, especially at mesh-frame contact.
- (e) If practicable, keep a set of wet sieves (each marked with a conspicuous W) apart from the dry series; theoretically they should be interchangeable in use, but under routine conditions, wet sieves are more liable to accentuated wear and tear, hence shorter life.
- (f) Where organic liquids and not water are involved, some form of closed-circuit system in flushing the sieves must be devised, unless undue wastage is to ensue. This is not difficult if supply and volume of liquid used in the process are strictly under control from the start and if steps are taken to see that the liquid collected in the 12-inch bowl beneath the sieve is easily and substantially recoverable¹.

(C) *Mechanical Shaking.* Mechanical shaking is unquestionably the answer to modern, industrial, routine particle-size analysis by use of screens, if only as a well-proven labour and time saver. There are several designs of apparatus for this purpose on the market, but in effect they operate on one or other of two main principles, viz., imitation of hand-sieving by which the required circular rotation of the sieve-nest is achieved to accompaniment of regularized vertical tapping from above; or electrically powered, vibrators (some are suspended models) which act on what might well be termed the 'tuning-fork' principle. In the former category, as one example, is the popular 'Ro-Tap' shaker electrically, also hand-driven², while the vibratory pattern is represented by such laboratory shakers as 'Hummer', 'Leahy No-Blind', etc. The popular 'Inclyno' test sieve shaker is essentially a gyratory model³.

It is not the intention here to discuss details of various types of mechanical apparatus for automatic laboratory screening extant, since full particulars of their construction, capabilities, performance and maintenance are readily available from the respective manufacturers.

The Ro-Tap shaker is built for use with 8-in. diameter test-sieves and takes up to six B.S. sieves with 2-in. clearance above gauze; some sieves are made with less clearance above gauze, when seven in a nest is practicable, allowing in each case for cover and pan. This is a very robust machine and will stand up to a great deal of hard wear.

¹ B.S.1796 : 1952, clause 6b, p. 9.

² International Combustion Ltd., London; W. S. Tyler Co., Ohio, U.S.A.

³ Manufactured by Pascall Engineering Co. Ltd., Crawley, Sussex.

The Inclyno shaker can be made to accommodate 6, 8, 12 and 18 in. diameter sieves and is supplied complete with motor and in-built automatic time-switch covering test periods up to one hour. The merit of this apparatus is its adaptability and inclusion of a noise-absorbing table.

MISCELLANEOUS METHODS OF PARTICLE-SIZE DETERMINATION

In this chapter on mechanical analysis, methods of determining particle-size distribution have embraced such processes as air-permeability (surface-area measurements), elutriation by air and water, sedimentation and sieving, all falling within the conventional scope of the subject. There exist, however, other techniques having much the same end in view, but implying entirely different modes of approach to the problems involved. First and for a long time foremost, are optical methods including microscopy¹; next, highly specialized, up-to-date procedures concerned with properties of light scattered or transmitted by suspensions of particles without actual formation of images²; and then there is the invaluable modern weapon of electron microscopy, without which our knowledge of sub-microscopic particles would indeed be scanty³.

Perhaps of all these techniques, ordinary microscopical (petrographic) examination of different particle-size fractions, realized by one or other procedure in mechanical analysis, is still the most complementary to such procedure. This aid is invariably called upon as a second opinion when it is found desirable to check up on efficiency of any physical operation concerned, likewise on accuracy of results thereby achieved. Microscopical measurement of particle-size is discussed elsewhere in this book (see Appendix to this Chapter p. 191, also Ch. VI).

For this present section, is reserved brief descriptions of certain methods applied to special cases in particle-size research, which are certainly not optical; nor do they follow any traditional lines of investigation normally pursued in mechanical analysis as such

β -Back-Scattering. In this atomic age, is a fitting and novel contribution to determination of particle-size, based on a complex process, but harnessed in such a manner by P. Connor, W. H. Hardwick and B. J. Lundy (Atomic Energy Research Establishment, Harwell), that it obviously possesses great potential possibilities of further development⁴. It is described as 'a cumulative

¹ Ch. VI.

³ Ch. XIV.

² R. D. Cadle, *op. cit.*, pp. 265 *et seq.*

⁴ *Journ. Appl. Chem.*, 9, 1959, p. 525.

method of particle-size analysis . . . wherein the mass deposited from an homogeneous suspension by gravitational or centrifugal force is determined by a β -back-scatter thickness measurement technique. The method is applicable to compounds having an effective atomic number greater than 16, and comparisons of results obtained by this and other methods for thorium, uranium, zirconia and lithopone powders are given' and, incidentally, found on the whole to be most satisfactory relative to results on similar materials obtained, for instance, by the Andreasen pipette or photo-extinction sedimentometer.

While, as postulated, β -back-scattering is restricted to compounds of effective atomic number > 16 , the authors claim these important advantages:

- (a) Settling is studied remotely;
- (b) no disturbance of suspension by sampling devices;
- (c) response instantaneous and free of inertial effects;
- (d) measurements are directly proportional to mass; and not such properties as projected area;
- (e) it is applicable to opaque systems;
- (f) sedimentation can be followed through both gravitational and centrifugal range on the same sample;
- (g) radiation hazard is very small compared with radioactive methods using γ -activities;
- (h) no neutron irradiation is necessary;
- (i) the apparatus possesses the same components as used in a radio-metric sedimentometer and is readily convertible.

The paper gives full details of the experimental apparatus involved, relevant count rate and energy of back-scattered radiation, calculation of results, comparative data with other methods of determining particle-size, and concludes with some useful references to the literature.

Bulk Density. F. S. Sinnatt and L. Slater¹ developed what is called the Bulk Density method of determining particle-size, based on the premise that with powders falling under controlled conditions on to a flat surface, bulk density of the resulting mass decreases with decreasing particle-size. R. D. Cadle describes the process: 'The powder is poured through a chute and allowed to fall into a cup of known volume. The excess powder is scraped off the top of the cup which is then weighed. The method is strictly empirical and must be calibrated for each type of powder used. This is accomplished by means of a series of powders of the same material but differing in mean particle size. A mean particle size, such as the surface mean diameter, is determined for each member of the

¹ *Fuel*, 2, 1932, p. 2.

series by some independent method. Particle size is then plotted against the bulk density¹.

The method is claimed to be rapid, easy to carry out and needs only simple apparatus. H. E. Rose, however, has criticized this technique in certain aspects of its application².

Diffusion Battery. The basic principle underlying use of this apparatus for particle-size determination is variation of diffusion rate of spherical colloidal particles from a liquid suspension into water, with size of these particles. Its application lies largely in the field of colloidal chemistry, but, by adaptation, particle-size up to 0.3μ in diameter has been successfully determined. Advantages of this diffusion battery method are: particles can be measured without collection; it is rapid; no lower limit to size which is measurable. Disadvantages: the method is generally inapplicable to particles $> 0.1\mu$ diameter and average size rather than size-distribution is the end-point³.

Electronic Size-Analysis. R. H. Berg, in a Symposium on Particle Size Measurement (1958)⁴ described a system of electronic size analysis of subsieve particles by flowing through a small liquid resistor. It is, he says, in the synopsis to his paper, '... basically a new principle of particle content and size analysis. . . . The method is applicable to sizes ranging from below 0.6μ to over 200μ . A suspension of particles in conductive liquid flows through an aperture with simultaneous flow of electrical current, resulting in a series of electrical pulses, each pulse being proportional in magnitude to the volume of the particle causing it. The pulses are amplified, scaled and counted to provide direct data for plotting cumulative particle frequency against particle size. Potentials and limitations are discussed, and methods of calibration, sample preparation, and data reduction are emphasized.'

Electrostatic Particle Counter. Devised by A. C. Guyton^{5,6} and is essentially an electrostatic apparatus for counting and determining

¹ *Op. cit.*, p. 294.

² *The Measurement of Particle Size in Very Fine Powders*, (Constable, London), 1953.

³ J. W. Thomas, The Diffusion Battery Method for Aerosol Particle Size Determination, ORNL 1648, *Instrumentation*, 5 January 1954; W. C. de Marcus and J. W. Thomas, Theory of a Diffusion Battery, ORNL 1413, *Instrumentation*, 16 October 1952; R. D. Cadle, *op. cit.*, p. 289.

⁴ Special Technical Publication No. 234, A.S.T.M., 1958, p. 245. The instrument is marketed by Coulter Electronics Inc., Chicago, Ill., U.S.A., and Coulter Electronics Ltd., London.

⁵ *Journ. Ind. Hyg. Toxicol.*, 28, 1946, p. 133.

⁶ For more details on this technique and those concerned with diffusion, sonic methods and bulk density, the reader is referred to R. D. Cadle, *op. cit.*, p. 287.

particle-size in an aerosol. It applies to particles $> 3\mu$. F. J. Gucker, Jr., and C. T. O'Konski¹ suggested an amended mechanism for operating the electrostatic counter; further, that sensitivity of the apparatus could be improved, whereby particles of 1μ size could be counted.

Sonic Methods. R. D. Cadle provides a lucid summary of the theoretical basis of equipment designed and used for particle-size estimations by this fascinating technique, one which, but for certain complications in manipulation, would appear to have encouraging possibilities for future development. He says: '... Particles suspended in air which is subjected to an intense sound field tend to follow the air molecules and vibrate with the sound wave. Very small particles vibrate with the full amplitude of the wave; larger particles lag behind and very large ones do not vibrate at all. The ratio of the amplitude of vibration of the particle x , to that of the sound wave, x_0 , is a function of the size of the particle².' For apparatus and procedure to determine this relationship, x/x_0 , the reader is referred to the authorities cited below^{3,4}.

GEOLOGICAL (PETROLOGICAL) CLASSIFICATION OF SEDIMENTARY ROCK-PARTICLES

In spite of certain ambitious alternatives, a few of them discussed in the sequel, the truly petrological classification and interpretation of particle-size distribution in a given sediment, originally defined by P. G. H. Boswell as long ago as 1918⁵, has withstood the test of time and is still, at least in this country, a conventional way of expressing results of mechanical analyses. The system was based on exhaustive research into British sediments and their mechanical constitution; it survives today largely because of its simplicity as a fundamental yardstick by which results of contemporary investigations in the same field of enquiry can be easily compared and measured. Any system of classification applied to sedimentary

¹ *Chem. Revs.*, **44**, 1949, p. 373.

² *Op. cit.*, p. 292.

³ H. M. Cassel and H. Schultz, *A Sonic Method of Determining Particle Size in Aerosols*. In L. McCabe, ed., *Air Pollution*, (McGraw-Hill, New York), 1952.

⁴ F. J. Gucker, Jr., *Determination of Concentration and Size of Particulate Matter by Light Scattering and Sonic Techniques*, *Proc. 1st Nat. Air Pollution Symp.*, Stanford Research Inst., Stanford, Calif., 1949.

⁵ *British Resources of Sands and Rocks used in Glass Making*, (Longmans, Green, London), 1918, p. 13. Also by the same author, *British Resources of Refractory Sands for Furnace and Foundry Purposes*, (Taylor and Francis, London), 1918, p. 13.

rocks, more particularly unconsolidated facies, must not only be workable from a geological or engineering standpoint, but it must automatically portray a convincing mental picture of how constituent particles in such rocks are internally arranged to form the familiar types, gravel, sand, silt, clay, etc., as recognized both in outcrop and in laboratory.

Criticisms of the Boswell classification of particle-size are mainly that the dividing line between very coarse sand and gravel (> 2 mm.) is set too low; *i.e.* to the eye, stuff as small as 2 mm. and just over, is more likely to be termed 'grit' than gravel, especially in the field. Again, the soil chemists place the upper limit of their clay particles at 2μ (Boswell's value is 10μ), and they are prone to think of all clay material as soil, where particle-sizes are more realistically conceived in terms of millimicrons ($\mu\mu$). At the other extreme, lack of any maximum size-limit to 'gravel' as such in the classification, poses a question: when does a mass of stones cease to be 'gravel' and become 'shingle', 'large pebbles' or even 'boulders'? C. K. Wentworth¹ attempted to remedy this alleged deficiency and with some success, particularly in the United States, where his classification, including as it does rudaceous constituents, has long been a conventional and popular mode of classifying components of sedimentary rocks.

Here, then, is the Boswell system:

SIZE-LIMITS OR GRADES	
<i>Diameter mm.</i>	<i>Rock-type and Symbol</i>
> 2	Gravel (G)
1-2	Very Coarse Sand (VCS)
0.5-1.0	Coarse Sand (CS)
0.25-0.5	Medium Sand (MS)
0.1-0.25	Fine Sand (FS)
0.05-0.1	Superfine Sand or Coarse Silt (s)
0.01-0.05	Silt (s)
< 0.01	Clay or Mud (c)

The Wentworth classification favours millimetre, and fractional millimetre size-limits in the lower and upper grades, which are

¹ Relevant papers by this author are: A Scale of Grade and Class Terms for Clastic Sediments, *Journ. Geol.*, 30, 1922, p. 377; Methods of Mechanical Analysis of Sediments, *Univ. Iowa Studies in Nat. Hist.*, 11, 1926, p. 50; Studies of Coarse Sediments, *Nat. Res. Council, Rep. Comtee. Sedimentation*, 1928; Method of Computing Mechanical Composition Types in Sediments, *Bull. Geol. Soc. Amer.*, 40, 1929, p. 771; The Terminology of Coarse Sediments, *Bull. Nat. Res. Council Rep. Committee Sedimentation*, 98, (1932-34), p. 225.

neither so easily remembered nor, for that matter, visualized as the decimal divisions employed in Boswell's scheme.

SIZE-LIMITS OR GRADES	
<i>Diameter mm.</i>	<i>Rock-Type</i>
> 256	Boulder
256-64	Cobble
64-4	Pebble
4-2	Granule
2-1	Very coarse sand grain
1- $\frac{1}{2}$	Coarse sand grain
$\frac{1}{2}$ - $\frac{1}{4}$	Medium sand grain
$\frac{1}{4}$ - $\frac{1}{8}$	Fine sand grain
$\frac{1}{8}$ - $\frac{1}{16}$	Very fine sand grain
1/16-1/256	Silt particle
< 1/256	Clay particle

In soil technology, the position is far from being satisfactory, since there are in existence several different proposed classifications of soil particle-size. In this country, what is known as the M.I.T. System¹ is adopted by the British Standards Institution² and in most engineering problems concerning soil-particles, these size-limits hold:

PARTICLE-SIZE DISTRIBUTION	
<i>Diameter mm.</i>	<i>Rock-Type</i>
> 2	Gravel
2-0.6	Coarse sand
0.6-0.2	Medium sand
0.2-0.06	Fine sand
0.06-0.02	Coarse silt
0.02-0.006	Medium silt
0.006-0.002	Fine silt
< 0.002	Clay

A few examples of variations from the above classification will serve to illustrate existing confusion in this matter:

¹ Massachusetts Institute of Technology (M.I.T.).

² B.S.1377 : 1948, p. 40.

PARTICLE-SIZE-DISTRIBUTION ¹	
<i>Diameter mm.</i>	<i>Rock-Type</i>
2-0-0.2	Coarse sand
0.2-0.02	Fine sand
0.02-0.002	Silt
-0.002	Clay

The International scheme is as follows²:

PARTICLE-SIZE DISTRIBUTION	
<i>Diameter mm.</i>	<i>Rock-Type</i>
> 2	Gravel
2-0-0.2	Coarse sand
0.2-0.02	Fine sand
0.02-0.002	Silt
< 0.002	Clay

What is known as the Continental scheme is a little more comprehensive:

PARTICLE-SIZE DISTRIBUTION	
<i>Diameter mm.</i>	<i>Rock-Type</i>
> 30	Stones
30-15	Coarse gravel
15-5	Medium gravel
5-2	Fine gravel
2-1	Very coarse sand
1-0.5	Coarse sand
0.5-0.2	Medium sand
0.2-0.1	Fine sand
0.1-0.05	Coarse Mo*
0.05-0.02	Fine Mo
0.02-0.006	Coarse silt
0.006-0.002	Fine silt
< 0.002	Clay

* Scandinavian term for intermediate particle-size range between fine sand and silt.

¹ C. E. Marshall, *Mineralogical Methods for the Study of Silts and Clays*, *Zeit. Krist. (A)*, **90**, 1935, p. 8.

² R. Glossop and A. W. Skempton, *Particle Size in Silts and Sands*, *Journ. Inst. Civ. Eng.*, **25**, 1945, p. 81. For International, Continental and U.S. Public Roads Administration Systems, see also P. L. Capper and W. F. Cassie, *The Mechanics of Engineering Soils*, (Spon, London), 1949, p. 37.

Finally, the scheme used by U.S. Public Roads Administration is interesting because of its inclusion of 'colloids'¹:

PARTICLE-SIZE DISTRIBUTION	
<i>Diameter mm.</i>	<i>Rock-Type</i>
> 2	Gravel
2-0.25	Coarse sand
0.25-0.05	Fine sand
0.05-0.005	Silt
0.005-0.001	Clay
< 0.001	Clay (Colloids)

R. Glossop and A. W. Skempton have discussed these systems of soil particle-size classification, especially in relation to the physical properties of individual fractions and they reach the conclusion that the B.S. (M.I.T.) classification is the most satisfactory for engineering purposes, because the dividing lines between the limiting sizes correspond to observed changes in properties of the soil itself².

The various methods of recording results of mechanical analyses of sediments are discussed in the sequel (p. 183).

Where the Boswell scheme of particle-size classification is adopted, it may be useful to know the B.S. sieve numbers which correspond approximately to the main divisions in that classification.

<i>Size Range</i>	<i>B.S. Sieves</i>
> 2	> 8
1.0 - 2	16-8
0.5 - 1.0	30-16
0.25-0.5	60-30
0.1 - 0.25	150-60
0.05-0.1	300-150

Where the Wentworth scheme of particle-size classification is adopted, the corresponding A.S.T.M. (U.S. Standard) sieve series, are shown in the table on page 183.

If required, the corresponding B.S. sieves can be found from the data summarised on p. 167.

¹ See P. L. Capper and W. F. Cassie, *op. cit.*, p. 37.

² *Op. cit.*, 1945.

<i>Size Range mm.</i>	<i>Rock Type</i>	<i>A.S.T.M. mesh</i>
+4	Pebble	—
4-2	Granule	5-8
2-1	Very coarse sand	10-16
1- $\frac{1}{2}$	Coarse sand	18-30
$\frac{1}{2}$ - $\frac{1}{4}$	Medium sand	35-50
$\frac{1}{4}$ - $\frac{1}{8}$	Fine sand	60-100
$\frac{1}{8}$ - $\frac{1}{16}$	Very fine sand	120-200
$\frac{1}{16}$ -1/256	Silt	230
-1/256	Clay	—

EXPRESSION OF RESULTS OF MECHANICAL ANALYSES

There exist almost as many ways of recording results of mechanical analyses of sediments as there are of classifying them geologically in terms of their inherent particle-size distributions, as may be evident from foregoing paragraphs. An urge to invent new and sometimes quite unnecessarily elaborate forms of portraying these analytical data was one to which many enthusiastic workers in sedimentary petrography, at least in the earlier days of its evolution, succumbed without, however, probably foreseeing the consequences; some of their ideas lacked permanent appeal and, during the course of time, were just relegated to forgotten archives. Perhaps this is a warning (or is it a challenge?) to contemporary students of this subject, but experience does tend to show that the simpler, straightforward, long-established modes of expression of results of mechanical analyses, by whatever means they may have been realized, have everything to commend them from both academic and applied scientific viewpoints.

The first example may be taken direct from a laboratory notebook and is self-explanatory.

Test No. ——— *Date* ———

Weight of sample submitted: 12 Kg.

Weight of quartered sample taken for sieve analysis: 100 g.

<i>B.S. Sieve</i>	<i>Weight retained g.</i>
7 mesh	Nil
14 "	0.2
25 "	2.0
52 "	34.5
72 "	27.4
100 "	28.9
200 "	4.0

Results expressed as percentages between sieves:

				<i>Sample</i>
Retained on	7	mesh	B.S. sieve	Nil
	14-7	"	"	0.2
	25-14	"	"	2.0
	52-25	"	"	34.5
	72-52	"	"	27.4
	100-72	"	"	28.9
	200-100	"	"	4.0
Passing 200 mesh B.S. sieve				3.0
Total				100.0

Results expressed as cumulative percentage passing B.S. sieves:

<i>B.S. Sieve</i>	<i>Sample</i>
7 mesh	100.0
14 "	99.9
25 "	97.8
52 "	63.3
72 "	35.9
100 "	7.0
200 "	3.0

In this form of report, the sign + indicates 'on' or 'retained' and - 'through' or 'passing'. Thus '+200-100 B.S. sieve' (the usual way of recording in this manner), means the sieve-fraction retained on a 200 B.S. sieve and passing 100 B.S. sieve; this is conveniently abbreviated to '200-100', and is the 'percentage between sieves'.

The British Standard method of reporting results of a sieve analysis is set out in much greater detail and is quoted here verbatim¹:

<i>Fractional percentages</i>	<i>Weight</i> %
Oversize on 72 mesh B.S. test sieve	0.4
Through 72 mesh B.S. test sieve, on 100 mesh B.S. test sieve	1.0
Through 100 mesh B.S. test sieve, on 150 mesh B.S. test sieve	6.8
Through 150 mesh B.S. test sieve, on 200 mesh B.S. test sieve	11.6
Through 200 mesh B.S. test sieve (including loss of 0.4%)	80.2
Total	100.0

¹ Reproduced by permission from B.S.1796 : 1952, Methods for the Use of B.S. Fine-Mesh Test Sieves, p. 13.

<i>Cumulative percentage undersize</i>	<i>Weight %</i>
Through 72 mesh B.S. test sieve	99.6
Through 100 mesh B.S. test sieve	98.6
Through 150 mesh B.S. test sieve	91.8
Through 200 mesh B.S. test sieve (including loss of 0.4%)	80.2

'The report should state in addition weight of sample, the method of sieving employed, the duration of the test and remarks on any unusual feature encountered, and any treatment or special method applied.'

Using the Boswell classification¹ (p. 179) two methods are recommended, one arbitrary, using symbols for the different rock-types, the other, graphical. In the former case, mechanical analysis of a sand from the Red Crag at Foxhall, Suffolk, has this expression:

VCS CS MS FS s C S

11.8 44.1 41.5 2.2 0.2 0.2 99.6

where VCS = very coarse sand, CS = coarse sand, MS = medium sand, FS = fine sand, s = silt, c = clay and S = total sand-grade, *i.e.* > 0.1 mm. diameter. This is a conveniently shortened form of recording results where a large number of analyses are involved².

The graphical method, *i.e.* plotting cumulative percentages of the different grades against the diameter of the particles in the grades, is the method favoured by P. G. H. Boswell, who says: 'The expression of mechanical analyses in the form of curves brings out contrasts and similarities in sediments more graphically than does the use of space (*e.g.* "strip" or "butterfly") diagrams³.' In Fig. 14 are reproduced three representations of mechanical analysis of typical sand and clays, taken from his memoir and which are to a large extent self-explanatory⁴. In this example, as in fact with most forms of graphical expression of results of mechanical analysis, the horizontal scale is proportional to the logarithms of the diameters quoted, so as to keep the scale representing the several grades within convenient compass.

A somewhat similar chart for recording sieve analysis results is recommended by the British Standards Institution and is reproduced here (Fig. 15); the vertical scale of this chart is an arithmetic scale and the horizontal scale is logarithmic⁵.

¹ P. G. H. Boswell, *op. cit.*, (Glass sand Memoir), pp. 13, 28.

² *Op. cit.*, p. 13. ³ *Op. cit.*, p. 28.

⁴ *Op. cit.*, p. 30, Fig. 5.

⁵ B.S. 812:1951, p. 22. (Revised 1960). (Reproduced by permission of the British Standards Institution.)

For graphical work with B.S. fine mesh sieves, logarithm of aperture is an easy value to plot because apertures of consecutive sieves are in the ratio $\sqrt[3]{2}:1$; thus logarithms of apertures are in arithmetical progression and sieves are consequently equally spaced. It is not quite so straightforward, however, with B.S. medium and coarse sieves, because spacing these sieves can become complicated unless certain sieves are omitted. As L. J. Chalk has pointed

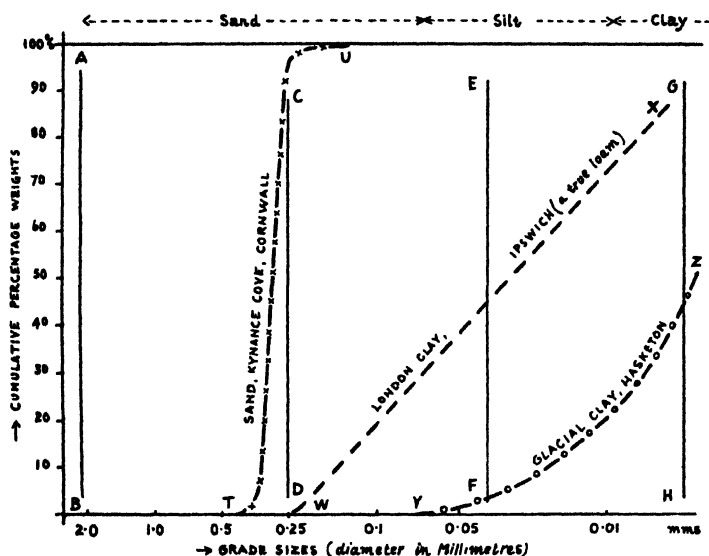


FIG. 14. Mechanical Analyses of Sediments: Graphical Representation (after P. G. H. Boswell).

AB = pure gravel.

CD = pure sand.

EF = pure silt.

GH = pure clay (all ideal).

TU, WX, YZ = curves of three British sediments subjected to mechanical analysis.

out: 'The sieves recommended for graphical work are 200, 100, 52, 25, 14, 7, $\frac{3}{16}$, $\frac{3}{8}$, $\frac{1}{2}$, $1\frac{1}{2}$ in., having apertures in the ratio of 1 : 2 : 8, etc. Alternatively any available B.S. sieves may be employed¹ . . . ' providing that a suitable chart is used, *e.g.* that originally included in B.S.812 : 1938, but replaced by the simpler form figured here on p. 187². It will be readily seen that this way of expressing results has the advantage of plotting logarithms of apertures, instead of actual aperture-sizes, to prevent 'bunching' of sieves at one end of the graph.

¹ *Sedimentary Petrography*, 3rd ed., 1940, p. 92.

² B.S. 812: 1951, Fig. 5. Also B.S. 812: 1960, Fig. 3.

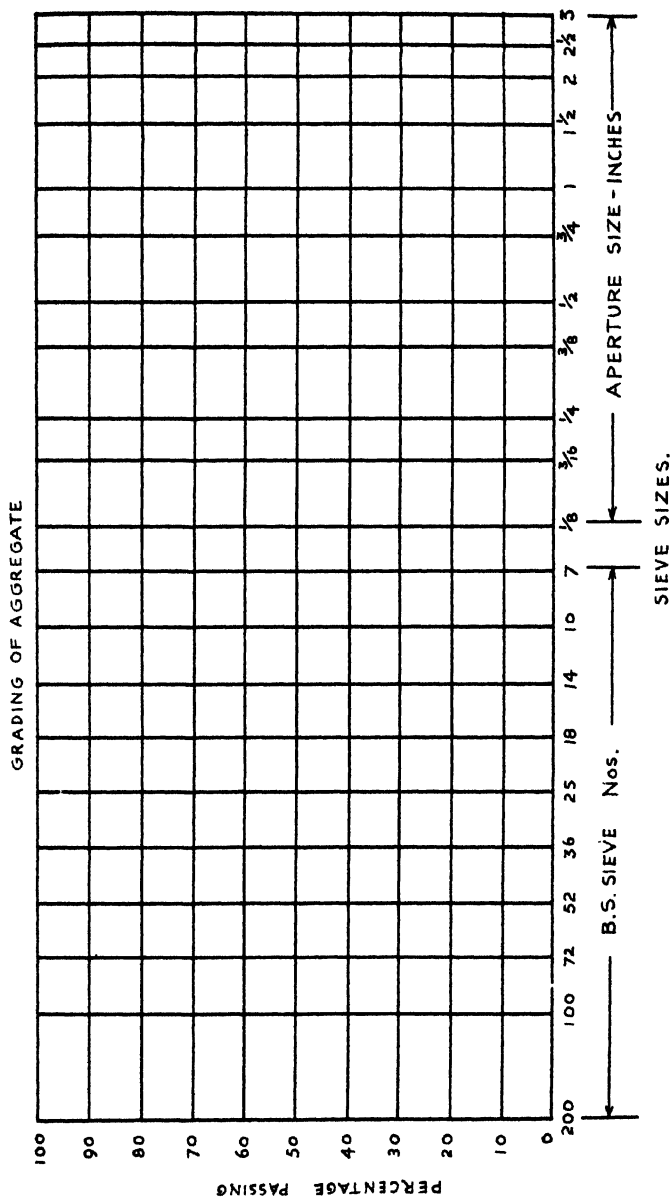


FIG. 15. Chart for recording Sieve Analysis Results. (British Standards Institution).

Apart from curves, many workers, especially in the United States, favour the use of histograms or triangular diagrams by which, they claim, particle-size distribution can be more easily visualized.

Histograms are a form of block diagram which can be constructed on ordinary graph paper¹. Each grade percentage is depicted by means of rectangular blocks, whose base represents limiting sieve-sizes or grade dimensions and height is percentage of such sizes. Fig. 16A illustrates the kind of diagram involved.

In the triangular diagram, an equilateral triangle, with usually 3-inch sides is divided into smaller triangles, as shown in Fig. 16B; it permits expression of the mechanical characteristics of a sediment in terms of three components, sand at apex, silt at left-hand corner, clay at right-hand corner. In the example illustrated, a single point X, as marked on the diagram, means that the sample contains 30% sand, 30% silt and 40% clay. A three-dimensional diagram, e.g. a pyramid, permits plotting four components, for instance gravel in addition to the other three².

The triangular diagram can be extended to portray several mechanical analyses by the single point or number system on one chart; this is, perhaps, one of its more obvious advantages³. The method is also popular in soil technology, where it appears to be quite as effective as in other fields of investigation of fine sediments⁴.

Finally, there are various statistical devices used for comparison, description and expression of the mechanical properties (particle-size distribution) of sediments, which make strong appeal to those who are mathematically minded. To what extent they may now or ultimately replace existing forms of expression is a moot point. 'Statistical results certainly permit rapid and easy comparison of large numbers of sediments and render it simple to point out similarities and differences. What significances the results have in terms of environmental conditions remain to be determined. . . . Statistical studies certainly permit extensive use of mathematical formulae which are of interest to those who are

¹ L. Dryden, Cumulative Curves and Histograms, *Amer. Journ. Sci.*, **27**, 1934, p. 146; E. W. Galliher, Cumulative Curves and Histograms, *Amer. Journ. Sci.*, **26**, 1933, p. 475; C. K. Wentworth, Methods of Mechanical Analysis of Sediments, *Univ. Iowa Studies in Nat. Hist.*, **11**, 1926, p. 50; also Method of Computing Mechanical Composition Types in Sediments, *Bull. Geol. Soc. Amer.*, **40**, 1929, p. 771.

² W. H. Twenhofel and S. A. Tyler, *Methods of Study of Sediments*, (McGraw-Hill, New York), 1941, p. 119.

³ A. Holmes, *Petrographic Methods and Calculations*, (Murby, London), 1921, p. 226.

⁴ P. L. Capper and W. F. Cassie, *op. cit.*, 1949, pp. 38-39.

mathematically inclined. The writers have found these formulae of great interest, but not particularly useful so far as interpretation of the sediments are concerned¹.

FINENESS MODULUS

A. D. Abrams originally used the term fineness modulus to express fineness of concrete aggregates². Fineness modulus of a single particle is a logarithmic function of its diameter. He used A.S.T.M. sieves 100, 50, 30, 16, 8, 4, $\frac{3}{8}$, $\frac{1}{4}$, $1\frac{1}{2}$ in. sieves. B.S. equivalents are valid (see table on p. 167). Fineness modulus is obtained by summation of cumulative retained percentages on those sieves and dividing by 100. Fig. 16C shows fineness modulus (using B.S. sieves) which is a number proportional to the area under the grading curve. On this subject, L. J. Chalk has commented³: 'The fineness modulus was primarily devised for use with concrete aggregates substantially free from silt and fine particles. It could, however, be extended to include particles belonging to the clay and silt grades and thus meet the more general requirements of geologists. The fineness modulus does not in itself provide a means of expressing the grading of a sediment by a single figure, since two sediments with entirely different ranges of particle size may have exactly the same fineness modulus; but by including suitable upper and lower size limits of the sediment as suffixes to the modulus, this difficulty is to some extent overcome.'

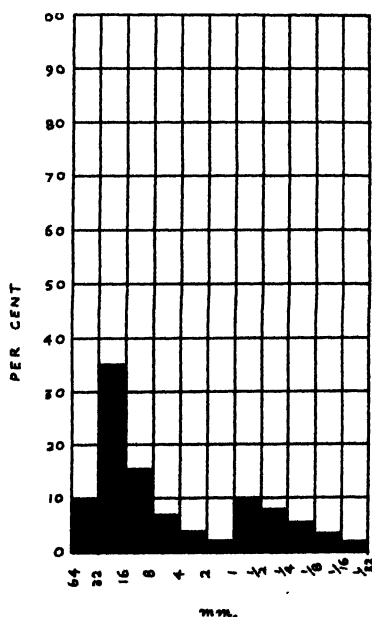


FIG. 16A. Histogram
(after C. K. Wentworth).

¹ W. H. Twenhofel and S. A. Tyler, *op. cit.*, p. 120.

² Structural Materials Research Laboratory, Lewis Inst., Chicago, *Bull.* 1, 1918.

³ *Sedimentary Petrography*, 3rd ed., 1940, p. 95.

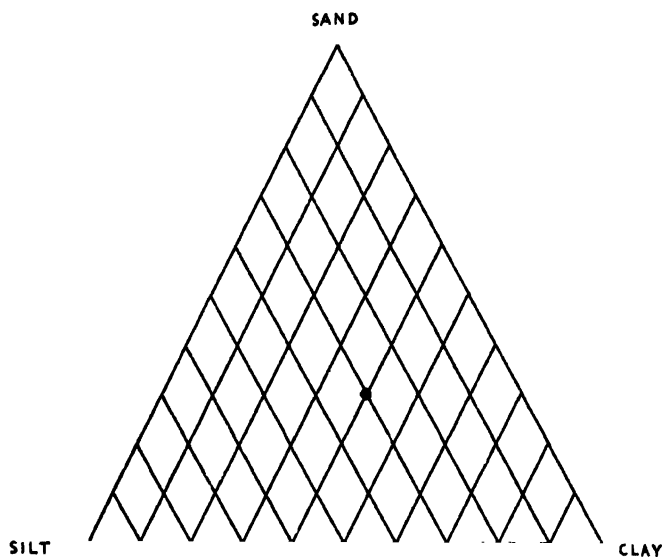


FIG. 16B. Graphical representation of character of sediments by triangular diagram. The composition of the sediments in terms of sand, silt, and clay is shown by the position of the black dot (after W. H. Twenhofel and S. A. Tyler).

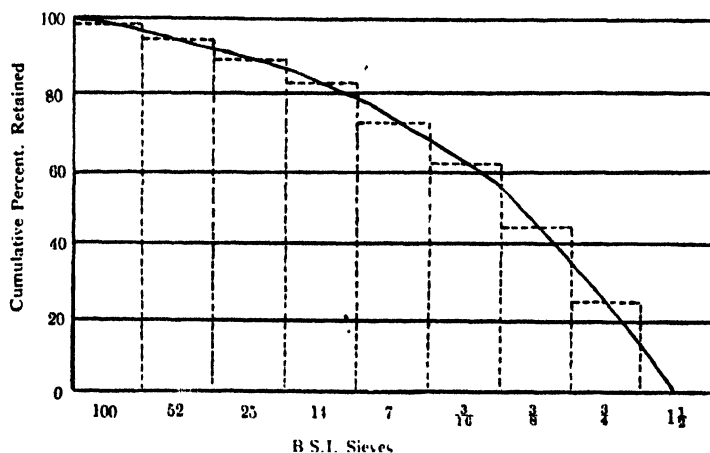


FIG. 16C. Fineness Modulus.

APPENDIX: ON PARTICLE-SIZE
AND MICROSCOPICAL MEASUREMENTS

Average particle-size of a mass of particles may be denoted in different ways, of which the following are examples:

- (i) As the arithmetical mean of the diameters of the particles:

$$D_1 = \frac{\sum nd}{\sum n}$$

- (ii) As a diameter which is directly related to the specific surface:

$$D_2 = \frac{\sum nd^3}{\sum nd^2}$$

- (iii) As a diameter related to the volume or weight distribution of the particles:

$$D_3 = \frac{\sum nd^4}{\sum nd^3}$$

- (iv) As the cube root of the arithmetical mean of the volumes of the particles, *i.e.* a diameter which can be used to determine the number of particles per g.:

$$D_4 = \sqrt[3]{\frac{\sum n^3 d}{\sum n}}$$

- (v) As the square root of the arithmetical mean of the surface of the particles, *i.e.* a diameter which can be used to determine the specific surface if the number of particles per g. is known:

$$D_5 = \sqrt{\frac{\sum nd^2}{\sum n}}$$

- (vi) As the arithmetical mean of the logarithms of the diameters of the particles, *i.e.*:

$$\log D_6 = \frac{\sum n \log d}{\sum n}$$

where D = average particle size (surface) of the whole sample,
 d = size of particles and n = number of particles.

Of the above, the expression (ii)

$$D_2 = \frac{\sum nd^3}{\sum nd^2}$$

i.e. the surface factor of G. J. Perrott and S. P. Kinney¹, is, according to L. J. Chalk², . . . the most suitable for sediments in that the average diameter so obtained is inversely proportional to the specific surface, *i.e.* the surface area of unit volume of the sediment'.

¹ The Meaning of Microscopic Measurement of Particle Size, *Journ. Amer. Ceram. Soc.*, 6, 1923, p. 417.

² *Sedimentary Petrography*, 3rd ed., 1940, pp. 114-17.

L. J. Chalk¹ originally described the routine followed in the author's laboratories regarding microscopical measurements of particle-size and although the subject is further discussed in Chapter VI on Microscopical (Optical) Examination of Sediments, it is considered appropriate that a *résumé* of the method should be given in the present chapter in the form of an Appendix.

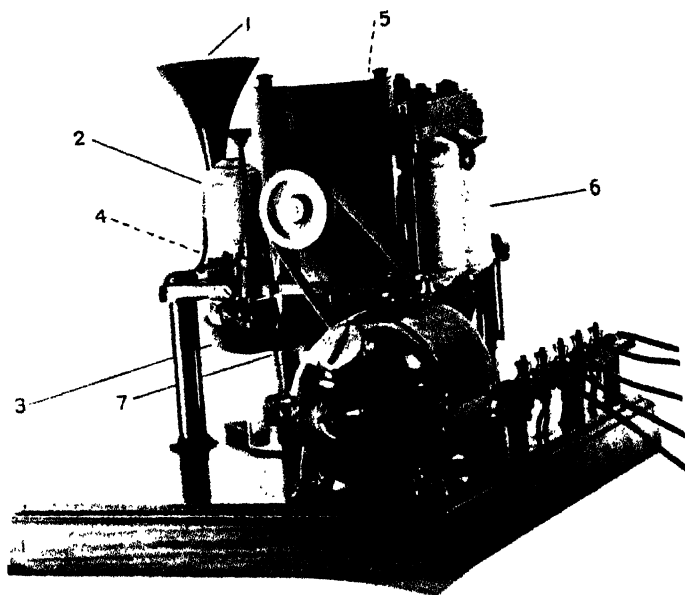
He says: 'The procedure given below has been found satisfactory for the examination of elutriation fractions containing particles greater than 10μ in diameter and consisting of approximately equi-dimensional particles. If the particles are not equi-dimensional, measurement becomes extremely tedious, as a large number of particles must be examined in all three dimensions. For measurement in two dimensions only, the diameter of an individual particle is taken as the side of a square equal in area to the projected area of the surface visible under the microscope. By the aid of a co-ordinate ruling in the eye-piece of the microscope, this operation can be carried out visually with great rapidity (Ch. VI, p. 220).

'The slide for measurement is prepared by placing approximately 1 mg. of the material on a clean microscope slide and dispersing it with a drop of alcohol to cover an area about $\frac{1}{2}$ in. square. When the alcohol has evaporated, an air-mount is made by sealing a cover glass in position with acetone-collodion. The slide is then placed under a microscope and the diameter of all the particles in the field determined by noting in turn the number of squares in an eyepiece co-ordinate ruling covered by each particle and taking the square root of this number. The result is usually estimated to the nearest unit or in certain instances to the nearest half unit and a particle recorded by means of a stroke in its appropriate classification (1, 2, 3, 4, 5, 6, etc.). It is quite unnecessary to attempt the exact sizing of each individual particle.'

'All the particles in one field are measured and the field then changed by moving the screw of the stage micrometer (p. 222), the process being repeated until at least 500 particles have been measured. The fields examined should be distributed as uniformly as possible over the total area of the slide and in the case of small particles (10μ) this necessitates the measurement of considerably more than 500 particles. Greater magnification is necessary if particles below 10μ in diameter are to be examined and can conveniently be obtained by passing a powerful beam of light through the microscope and projecting the image of the particles on to a suitably placed screen.'

'The microscope used in the author's laboratories and described on p. 214 has no petrological accessories, a $\frac{1}{4}$ inch objective and $\times 6$ ocular with a co-ordinate ruling generally being employed. A convenient size of co-ordinate ruling is that giving squares of apparently 0.01 mm. side when used with a $\frac{1}{6}$ th of an inch object glass, a $\times 6$ eyepiece and a standard length draw-tube. The special auxiliary micrometer (p. 222) fitted to the stage of the microscope permits successive transverse fields to be easily examined and also enables the co-ordinate ruling in the eyepiece to be readily calibrated. This auxiliary micrometer consists

¹ *Op. cit.*, p. 115.

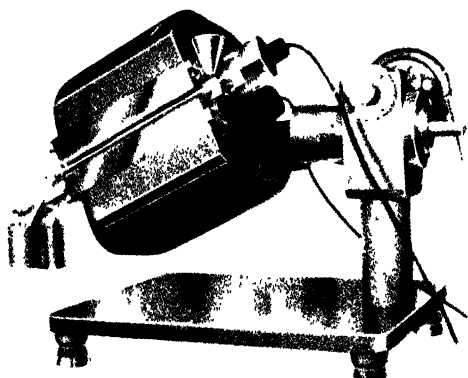


HALLIMOND ELECTRO-MAGNETIC SEPARATOR FOR MINERAL POWDERS.

- | | | | |
|---|---|---|---|
| 1 | Feed Hopper | 5 | Second Separating Magnet (hidden from view) |
| 2 | Magnet Operating Feed Valve | 6 | Final Separating Magnet |
| 3 | Conveyor Disc | 7 | Brush |
| 4 | First Separating Magnet (hidden from view). | | |

PLATE. 3

To face page 192



COOK MAGNETIC SEPARATOR.

Courtesy Chas. W. Cook & Sons Ltd., Birmingham, 72 B.V.

essentially of a supplementary stage which is moved in a dove-tailed slide by a screw of 1 mm. pitch. A drum divided into a 100 divisions is attached to one end of the screw and a vernier enables measurements of 1/10th of a division, i.e. 0.001 mm., to be carried out.'

'Calibration of the co-ordinate ruling is carried out in the following manner. A small scratch is made on a microscope slide which is placed on the stage and adjusted until the scratch is coincident with one of the lines in the co-ordinate ruling, when the reading on the drum is taken. The stage is then moved until the scratch is coincident with a line 10 or 20 divisions away from the first and another reading of the drum taken. From these two readings the apparent distance between the rulings can be calculated. Measurements are taken in all parts of the co-ordinate ruling and errors due to backlash (if any) are avoided by moving right across the field with the drum constantly turning in one direction. This combination of a co-ordinate ruling with a travelling stage micrometer is entirely suitable for particle size measurement.'

'An example of the calculation of the average diameter (surface) is set out below:

'Elutriation fraction 0.03-0.04 mm.

'Calibration of co-ordinate ruling: unit of length: $d = 9.6\mu$.

<i>No. of particles n</i>	<i>Size of particles d</i>	<i>nd²</i>	<i>nd³</i>	<i>Per cent. by surface</i>
53	1	53	53	0.5
48	2	192	384	2.0
184	3	1,656	4,968	17.4
301	4	4,816	19,264	50.6
97	5	2,425	12,125	25.5
8	6	288	1,728	3.0
2	7	98	686	1.0
693		9,528	39,208	100.0

'The average diameter (surface) of the fraction is given by:

$$\text{Average particle size } d_2 = \frac{\sum nd^3}{\sum nd^2} \times 9.6 = \frac{39,208}{9,528} \times 9.6 = 40\mu$$

'Assuming the particle size of all the fractions elutriated from a particular sediment can be measured in this way, the average particle size (surface) of the whole sediment may then be calculated from the formula:

$$\frac{W_1}{d_1} + \frac{W_2}{d_2} + \frac{W_3}{d_3} + \text{etc.} = \frac{100}{D_2}$$

where W_1, W_2, W_3 , etc. are the percentage weights of the elutriated fractions and d_1, d_2, d_3 , etc. their average particle sizes (surface) and D_2 the average particle size of the whole (surface).'

CHAPTER V

LABORATORY TECHNIQUE PART 3. FURTHER METHODS OF MINERAL CONCENTRATION

Magnetic Separation—Electro-magnetic Separation—Electrostatic Separation—Dielectric Separation—Vibratory Methods—Flotation Methods.

*

IN this chapter special methods for effecting heavy mineral concentration other than those concerned with heavy liquids and mechanical analysis are described. In general the methods are designed to meet particular cases and cannot be said to be universally applicable to all sedimentary rock-minerals; nor do they by any means supplant the simpler high-gravity liquid technique in mineral concentration.

MAGNETIC SEPARATION

In most cases this follows a preliminary concentration of heavy mineral with bromoform or other media, though exceptionally, *e.g.* with naturally panned material, a magnetic separation may be advantageous at the outset of examination.

Before commencing operations, the minerals to be searched with the magnet should be as dry as possible. For strongly magnetic species, such as magnetite, a permanent bar or horseshoe magnet will be found most effective. The minerals should be spread out uniformly on a flat, white (preferably glossy) surface and the magnet passed systematically just above (not within) the mass, which should constantly be turned over with a spatula to ensure thorough extraction.

For easy release of the magnetite or other mineral thus segregated, it is a good plan to hold over the pole piece(s) a small strip of thin tissue paper, which is easily detachable from the magnet and from which the extracted mineral will automatically drop once clear of the magnetic field.

Horseshoe magnets fitted with adjustable pole pieces (Fig. 17) give better results than ordinary bar or fixed pole horseshoe magnets, in that variation of the gap between the points creates a magnetic field of greater or lesser intensity, whereby less strongly magnetic minerals than magnetite may be segregated. Such magnets are of considerable use, especially in the field, when concentrating alluvial minerals. In this connexion J. D. Falconer¹ described a means of achieving a very strong magnetic field (when an electro-magnet is unavailable) consisting of four horseshoe magnets (with adjustable pole pieces) bound together.

For purposes of testing the efficiency of bar and horseshoe magnets (with and without adjustable pole pieces in the latter case), trials should be made with the following minerals purposely mixed to form a concentrate:

Almandine
Ilmenite
Magnetite
Monazite
Zircon

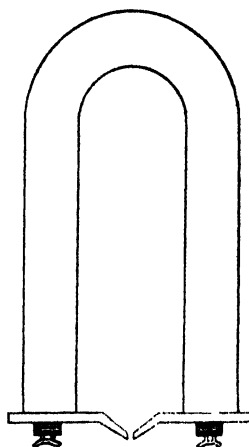


FIG. 17. Horseshoe Magnet with Adjustable Pole Pieces.

See also full list on p. 198.

ELECTRO-MAGNETIC SEPARATION²

Where provision for an electro-magnet can be made, this is a far more convenient and flexible apparatus with which to work, since magnetic intensity can be made to vary with the magnitude of the current used, with the distance between the pole pieces, or according to the space allowed between the ends of the pole pieces and the concentrate. In this way a concentrate, whose strongly magnetic minerals have already been abstracted with a bar or horseshoe magnet, may be divided into moderately magnetic, weakly magnetic, and non-magnetic crops; or, of course, the electro-magnet may be used for the entire separation. It will be found that repeated searching of the crops with the magnet is necessary to arrive at cleanly segregated groups, and the achievement of the four

¹ Nature, 78, 1908, p. 247.

² This, and the succeeding paragraphs on Electrostatic Separation, Dielectric Separation and Vibration Methods, are in part taken from *Alluvial Prospecting* by C. Raeburn and H. B. Milner (Murby, London), 1927.

distinct grades, strongly magnetic, moderately magnetic, weakly magnetic and non-magnetic, is not as easy as would appear at the outset, largely for the reason that the minerals themselves vary considerably in their magnetic properties, even similar species in the same concentrate.

'Electro-magnets are made to several designs, but the principle of all patterns is much the same. Fig. 18 shows one satisfactory type employed by the authors.

'The current is supplied either by an accumulator, suitable battery or direct from light or power supply, in which case an adequate resistance must be placed in the circuit. If electric lamps wired in parallel are used for this purpose, the resistance can be altered by

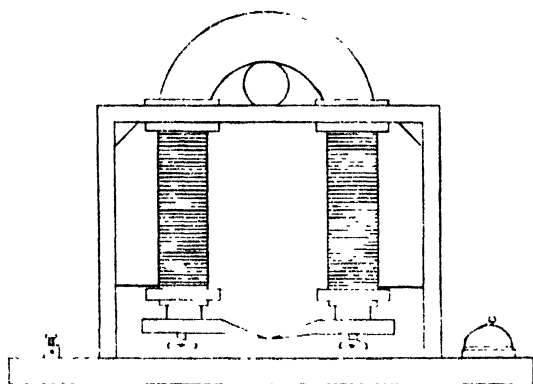


FIG. 18. Electro-Magnet.

decreasing or increasing the number in circuit, resistance (ohms) varying inversely, and current (amperes) directly as the number of lamps employed; the lamps should each be of similar candle-power or watts. Alternatively, a suitable rheostat may be used for controlling the resistance. The design of electro-magnet chosen will, to a great extent, depend on the nature of the separations which will commonly be made, the power available, and other local circumstances.'

Electro-magnetic separation of minerals in the laboratory was some years ago facilitated by A. F. Hallimond¹, who designed an instrument capable of dealing with the less magnetic minerals and of giving a clean separation. It has been found that commercial separators cannot easily be adapted to laboratory requirements, since normal practice in design of these is to interpose a conveyor

¹ An Electro-magnetic Separator for Mineral Powders, *Miner. Mag*, 22, 1930, p. 377.

between the pole pieces. Consequently, as soon as the scale of the plant is reduced it becomes impossible to incorporate a sufficiently strong conveyor without at the same time producing a wide gap in the magnetic circuit. The principle embodied in this type of laboratory separator is to feed the material directly beneath a double-pole magnet, both poles being above and close to the conveyor. When the magnet is above an opening in the surface of the conveyor, the magnetic material is discharged by interrupting the current. Pl. 3 shows details of the design of this separator.

Procedure is as follows: after grading, the mineral powder is placed in the feed hopper (1) which is closed by a valve. Beneath a small table there is a conveyor disc (3) which is rotated clockwise by a small motor. The disc is grooved near the outer edge and the material is carried in this groove. At intervals the groove is cut away, leaving four shelves with alternate gaps through which the magnetic material can be discharged. On rotation of the disc, the shelves pass beneath the hopper-mouth. At a given moment contact is made by a mercury tube switch operated from the central spindle (supporting the conveyor disc) and the armature of the feed valve is thus raised by the electro-magnet. A small quantity of material is in this way deposited on each shelf. The shelf then passes below a small single pole magnet (4) which removes any magnetite present, a large magnet (5) for garnet and a final magnet (6) for monazite. After discharge by interruption of the current of the magnetic fractions through their respective gaps into glass dishes below, the residue is finally passed under a brush which sweeps the bottom of the groove and carries the material into another glass dish. The operation can then be repeated immediately.

A more recent version of the magnetic separator 'is essentially a powerful Electro-Magnet, with pole pieces of special design, incorporating a feed hopper, a double track non-magnetic pan with Vibrator, a divided chute, and two collecting buckets'. This apparatus is supplied complete with resistance and ammeter and a rectifier unit is available for obtaining 110 Volts (d.c.) for the magnet coils. It incorporates a very sensitive control by means of special worm and wheel allowing easy setting of the magnets. It is claimed that separation with this apparatus is a simple matter and that if the minerals under investigation possess 'any magnetic properties at all, this machine will separate them'¹ (Pl. 4).

To avoid mis-identification of mineral grains which, after electro-magnetic separation, may have strayed into the wrong fraction, it is often desirable to be able to determine magnetic properties of individual grains. It may also be desirable to determine magnetic properties of single grains where an electro-magnet is not available. A simple device has been invented by F. Smithson² to achieve these

¹ C. W. Cook and Sons Ltd., Perry Bar, Birmingham 22B, England.

² A simple Method of Observing the Magnetic Properties of Mineral Grains, *Miner. Mag.*, 22, 1930, p. 419.

ends. A piece of cardboard approximately $1\frac{1}{2}$ in. \times $1\frac{1}{2}$ in. is folded at one end to give a square $1\frac{1}{2}$ in. \times $1\frac{1}{2}$ in. Two darning needles, after being heated to redness and allowed to cool slowly, are pushed through the fold of the card at about $\frac{1}{2}$ in. apart and secured by seccotine so that the points are close together. The needles are placed on a horseshoe magnet and a strong magnetic field thus achieved between the points. To facilitate operations several sets of needles should be prepared with varying distances between the points. These distances then should be marked on the card and also the letters 'N' and 'S', so that they are always placed on corresponding poles of the magnet. It is advisable to immerse the material to be tested in a liquid medium, *e.g.* benzol or bromoform. As the needle points approach the grains, their behaviour is observed under the microscope. The nature of the magnet used, distance between needle points, magnetic properties of the mineral, size of mineral grains and nature of the liquid medium employed, are all factors which will influence the behaviour of the grain under observation.

Whatever means are employed for segregating minerals according to their magnetic properties, for all practical purposes in sedimentary petrography a division into magnetic and non-magnetic crops normally suffices. Where it is a question of isolating a particular species, *e.g.* in sufficient amount for chemical analysis, then much narrower division is necessary, so that four crops at least are realized, *highly magnetic, moderately magnetic, weakly magnetic, non-magnetic*. With a powerful and sensitive electro-magnet, subdivisions within the second of these crops may occasionally be made in suitable circumstances, *e.g.* separation of garnet and ilmenite, both normally together in the 'moderately magnetic' crop.

The following is a list of minerals occurring in sediments which may be expected to reveal magnetic properties to a greater or lesser extent. The student is warned, however, that the same mineral may vary considerably in this respect according to composition and source of origin, *e.g.* almandine garnet which is moderately magnetic in some cases and only weakly so in others.

** Actinolite	** Diopside
*** Augite	** Epidote
*** Biotite	*** Garnet
*** Cassiterite	*** Glaucconite
** Ceylonite	*** Hematite
** Chlorite	*** Hornblende
** Chloritoid	** Hypersthene
*** Chromite	*** Ilmenite
*** Cordierite	**** Magnetite

** Marcasite	** Pyrolusite
** Monazite	**** Pyrrhotite
** Muscovite	*** Sphalerite
** Olivine	** Staurolite
*** Picotite	** Tourmaline

**** denotes strongly magnetic, separable with a bar magnet.

*** denotes moderately magnetic, separable with a horse-shoe magnet (adjustable pole pieces).

** denotes weakly magnetic (sometimes separable with a horseshoe magnet, adjustable pole pieces).

ELECTROSTATIC SEPARATION¹

'Minerals which are good conductors of electricity may often be extracted from a concentrate by means of a glass rod in which a charge is induced by rubbing with silk (+), or ebony or sealing-wax rubbed with catskin or rough flannel (—). The application of this well-known principle was developed in connexion with mineral separation by T. Crook many years ago². His apparatus consisted of two copper plates, one supported above the other; the upper one has its under-surface coated with a thin layer of shellac "which should be continued over the edge of the plate so as to form a narrow strip around the margin of the other face. At or near the edges of the shellac-covered face there should be insulating supports, which may conveniently be made of two narrow strips of glass cemented to the plate and coated with shellac". This upper plate, with its supports, is placed on a lower naked copper plate, on which the mineral grains are first placed. On charging the upper insulating plate with the aid of an electrophorus—providing the minerals and the whole apparatus are absolutely dry—the good conductors are attracted to the shellac-covered surface of the top plate, from which they are ultimately removed by lifting the plate and brushing the grains off the lower surface. In this way the non-conductors are left behind on the bottom plate; such a concentrate "can be finally cleaned as far as possible by the sealing-wax method, which offers fuller control". Electrostatic methods of separation are extremely useful in isolating such minerals as ilmenite, magnetite, wolframite, columbite and tantalite from cassiterite (sometimes a moderate conductor), quartz, zircon, monazite, apatite, etc.'

The following is a list of sedimentary rock minerals classified according to their relative electrical conductivities:

¹ C. Raeburn and H. B. Milner, *op. cit.*, p. 240.

² The Electrostatic Separation of Minerals, *Miner. Mag.*, 15, 1909, p. 260; 16, 1911, p. 109.

** Actinolite	*** Ilmenite
** Anatase	** Leucoxene
** Augite	** Limonite
** Biotite	*** Magnetite
** Brookite	*** Marcasite
** Cassiterite	*** Picotite
*** Cassiterite (ferriferous)	*** Pyrite
*** Chromite	** Pyrolusite
** Diopside	*** Pyrrhotite
** Glaucophane	*** Rutile (ferriferous)
*** Graphite	** Sphalerite
*** Hematite	** Titanite
** Hornblende	** Tourmaline
** Hypersthene	*** Wolframite

*** denotes good conductors easily attracted.

** denotes moderate conductors, attracted with difficulty.

DIELECTRIC SEPARATION¹

B. W. Holman some years ago carried out research on the Hatfield process of dielectric separation as a factor in mineral concentration². The following possibilities were investigated:

(i) The separation of good conductors from bad ones of low dielectric constant, *e.g.* finely disseminated zinc blende from galena, metallic silver from vein-material.

(ii) The separation of earthy minerals of low dielectric constant from one another or from gangue material, *e.g.* oxides of Ni, Co, U, V, Ce, Th, and such minerals as gadolinite, phenacite, carnotite, etc.

(iii) The treatment of tin ores, especially when cassiterite is of very fine grade.

(iv) The separation of heavy minerals from a concentrate of a particular species which is a good conductor or which possesses a fairly high dielectric constant, *e.g.* thorina and ceria from tin concentrate.

'It is apparent that under certain conditions the methods are applicable to mineral concentrates, especially if these are of fine grade. Briefly, the method consists in using a grating immersed in a suitable liquid (whose dielectric constant falls between that of the two minerals it is desired to separate); the parallel bars of the

¹ C. Raeburn and H. B. Milner, *op. cit.*, p. 241.

² *Mining Mag.*, 28, 1923, p. 267; *ibid.*, 30, 1924, pp. 132, 181; also *Bull. Inst. Min. and Metall.*, 1924, p. 335.

grating are alternately connected up to the two ends of an alternating current, 200–250 volts; the mineral possessing the higher dielectric constant is attracted to the bars, that with the lower dielectric constant being repelled. An example is furnished by quartz and cassiterite; the latter has a dielectric constant (50) and is attracted, while quartz (4.5) is repelled if the grating is immersed in aniline (7.3), amyl alcohol (16) or nitro-benzene (36). "Minerals which differ from one another in dielectric constant by as little as a whole unit can be so separated if their dielectric constants be below 60."

The following table of dielectric constants is quoted from Holman's paper:

TABLE I. DIELECTRIC CONSTANTS

Solids		Liquids	
Ebonite	2.5	Kerosene	2.0
Sulphur	3.0	Benzene	2.3
Quartz	4.5	Carbon disulphide	2.6
Rock Salt	5.6	Aniline	7.3
Fluorite	6.8	Acetylene tetrachloride	10.0
Calcite	7.5	Amyl alcohol	16.0
Mica	8.0	Ethyl alcohol	26.8
Blende	40.0	Ethylene dichloride	18.0
Cassiterite	50.0	Methyl alcohol	35.4
Magnetite	over 50.0	Nitrobenzene	36.0
Rutile	over 50.0	Water	70.0

It should be remembered that these figures vary with the frequency employed, also that, for some of them, different authorities give very different figures.

'For further particulars of this process, reference should be made to the papers cited.'

G. A. Berg¹ has suggested a slight modification of the technique of dielectric separation which he claims gives results more comparable with published constants than those normally obtained. He uses ordinary 60-cycle alternating current stepped up to 880 volts. This voltage is secured by an ordinary radio transformer. 'A 1-ampere fuse is placed in the primary circuit and a resistance of 2,000 ohms in the secondary circuit. Wires from the secondary circuit lead to needles mounted on an insulated pencil-like handle.' The space between the needle points provides the necessary electric field. The separation takes place in a small flat, glass container. The highly magnetic grains are previously removed from the sample with a magnet. Furfural and benzene are mixed in correct proportion to give a liquid medium of the desired dielectric constant and the needle points immersed therein. Those minerals which have a dielectric constant higher than the liquid medium are attracted by the

¹ Notes on the Dielectric Separation of Mineral Grains, *Journ. Sed. Pet.*, 6, 1936, p. 23.

electric field and those with a lower are repelled. Grains attracted can be transferred to a smaller glass dish in the large container. The needle points are then held in the liquid above the smaller container and subsequently drawn out of the liquid. The grains fall thus into the smaller dish. The smaller dish is then withdrawn with forceps and the grains washed with alcohol.

During the course of experimentation with various minerals and adopting this procedure, it was noted that time of immersion in the liquid medium had a definite effect on results obtained. This was especially marked in the case of glauconite, but no attempt was apparently made to determine the relation between time of immersion and the effect on dielectric constants of minerals.

S. R. Hudson¹, has more recently described the principles and properties of the Plate-Type Separator in which electrostatic separation depends on using differences in electrical properties of the mineral particles to be separated. This form of separator utilizes (a) conductance charging 'in which particles passed over a metal surface charged by induction are themselves charged by conduction from it', and (b) contact-potential or frictional charging 'in which particles acquire a charge while passing over a surface and maintaining frequent intimate contact with it'. See also relevant papers by F. Fraas and O. C. Ralston² and H. B. Johnson³.

VIBRATORY METHODS¹

'Some years ago a method was developed for separating certain minerals by induced vibrations, more particularly cassiterite, wolframite, columbite, etc., from vein-quartz or gangue (in the crushed state). The principle depends on imparting frequency to a sheet of paper or a thin metal plate on which the minerals have been placed. The paper or plate is held in suspension horizontally at one end by the left hand, and the necessary vibrations set up by regular tapping with a pencil or a hard instrument with the right hand; alternatively, a thin metal plate is clamped at one end and made to vibrate by resonance, using a tuning fork of suitable pitch; the frequency of vibration depends on the thickness of the plate and the point at which it is clamped. The method is not one of universal application, but with certain concentrates (only ascertainable by trial) it works well.

'When employing vibratory methods of concentration, it is found

¹ Recent Developments in Mineral Dressing, *Inst. Min. and Met.*, 1953, p. 335 *et. seq.*

² *Rep. Invest. U.S. Bur. Min.* 3667, 1942 and 4278, 1948.

³ *Trans. Amer. Inst. Min. Met. Eng.*, 134, 1939, p. 409.

⁴ C. Raeburn and H. B. Milner, *op. cit.*, p. 242.

that if a highly glazed paper or well-polished copper or brass plate be used, separation is considerably facilitated; also, minerals possessing a large surface-area in proportion to their thickness, *e.g.* mica, lag behind the more irregularly shaped (and often heavier) species; thus the method is useful for getting rid of excessive mica, light particles of foreign matter, dust, etc., though it should be pointed out that the principle involved in the latter cases is that of retardation due to friction rather than to the periodicity set up in the supporting medium and imparted to resonant grains.'

On a much larger scale, dry separation of minerals is illustrated by the concentration of ores by Pneumatic Tables following successful coal cleaning treatment by this method. Those interested should consult papers by E. A. Knapp¹ and E. A. Knapp and C. T. Sweet² and references therein cited.

FLOTATION METHODS

Water, oil and froth flotation methods of mineral concentration are well known in ore-dressing technique. Similar methods on a laboratory scale have from time to time been tried with mineral concentrates of small particle size, with varying degrees of success.

In industry, the term 'flotation', according to H. L. Sulman³ now has a limited application to ore-concentration processes by which particles are suspended in an aqueous ore-pulp and subsequently recovered in an air-bubble froth. There are, however, other methods which can be roughly classified into 'filming' processes, or those utilizing surface-tension effects at a water surface; 'oil-buoyancy' methods where oil is employed both as adhesive and buoyant medium for the particles separated; 'adhesion' processes dependent on adhesion between oil or grease and the separable particle; 'mineral froth' processes where the froth is produced by gases other than air and 'plus-pressure' methods based on the principle of generation of air-bubbles upon mineral and oiled particles by pressure differences.

Flotation methods are applicable to nearly all sulphide ores, minerals in which sulphur and graphite occur in practicable amounts, oxidized ores of lead and copper, oxide minerals (*e.g.* cassiterite), gangue minerals, etc.

In practice, froth flotation is achieved by agitating an aqueous ore-pulp (usually not less than 4 parts by weight of water to 1 of

¹ Concentrating Ores by Pneumatic Tables, Recent Developments in Mineral Dressing, *Inst. Min. and Met.* 1953, p. 299.

² Concentration of Eluvial or Co-Eluvial Deposits in Arid Areas, *op. cit.*, 1953, p. 313.

³ A Contribution to the Study of Flotation, *Trans. Inst. Min. and Metall.*, 29, 1919, p. 138.

ore) with the following reagents: a 'froth producing' material such as cresol, amyl alcohol or the soluble portion of an oil. This permits formation of an extensive froth by slight reduction of the surface tension of the water and the mineral particles attach themselves to the froth; a 'froth stabilizing' material (usually an insoluble oil) which is absorbed at the sulphide mineral surfaces and stabilizes the composite froth by increasing the water-mineral contact angle; a 'gangue modifying' substance, e.g. a mineral acid, alkali etc., which increases adhesion between gangue particles and water.

The results of flotation are explained by differences in the degree of 'wetting' by water or other liquids suffered by various substances. On withdrawal of a solid substance from a liquid, according to the nature of its surface it remains wet to a greater or lesser degree. Some substances appear to repel moisture and on extraction from liquid become more or less dry. Substances capable of complete wetting by a liquid become true suspensions therein. In the case of crushed ore and water, preferential wetting effects are not sufficiently marked to permit separation of sulphide minerals from gangue. The differences can, however, be intensified by addition of reagents and specific procedures and successful flotation thereby realized.

Until the early 1920's, only the bulk flotation of sulphide minerals had been achieved but, following the discovery that modifying, or conditioning, agents could be added to the ore pulp to depress particular minerals selectively, processes of 'differential' flotation were rapidly developed¹.

From then on, understanding of the mechanisms and physical-chemical reactions involved in flotation has continued to grow². Flotation processes now typically involve a 'pulp-conditioning' stage—i.e. preselection treatment, a 'collection' stage—demanding selective coating of a desired mineral, and, lastly, an 'aeration' (or 'frothing') stage, during which the selected mineral is floated off³. With the 'float' removed, the 'sink' can be conditioned anew preparatory to removal of another mineral, and so on.

Numerous collecting and frothing agents have been examined by research workers and many proprietary brands of such agents are readily available. With these to choose from, it is safe to say that a suitable combination for a particular mineral (and not necessarily a sulphide) can be found without great difficulty, provided comminution before treatment has 'freed' the desired particle from its mineral association.

¹ E. J. Pryor, *An Introduction to Mineral Dressing*, (Mining Publications, London), 1955.

² K. L. Sutherland and I. W. Wark, *Principles of Flotation*, 2nd. ed., *Aust. Inst. Min. Metall.*, 1955.

³ A. F. Taggart, *Elements of Ore Dressing*, (Wiley, New York), 1950.

Normally apparatus used for flotation processes is designed to treat fairly large quantities of ore. H. Sulman and F. K. Picard¹, however, described a unit which has been designed for laboratory purposes. The scale of apparatus does not in any way affect the principles of flotation provided it is capable of accurate quantification of reagents added to the ore-pulp, addition of given quantities of oil in the form of a dilute emulsion and dissemination of minute air-bubbles through the pulp. These requirements are met in the apparatus described, which can handle a minimum quantity of 10 g. of ore and give results comparable in accuracy with those obtained on bulk quantities of material in large units. Since 1923, many pieces of laboratory equipment have been designed to aid laboratory testing work², while manufacturers of commercial flotation cells can generally supply laboratory-scale units of their own design³.

¹ Apparatus for Small-Scale Flotation Tests, *Trans. Inst. Min. Metall.*, **32**, 1923, p. 124.

² A. F. Hallimond, Laboratory Apparatus for Flotation Tests, *Min. Mag.*, **70**, 1944, p. 87; The Role of Air in Flotation at Great Dilution, *Min. Mag.*, **72**, 1945, p. 201; E. J. Pryor and K. B. Liou, A Simple Flotation Cell, *Trans. Inst. Min. Metall.*, **58**, 1948-49, p. 85.

³ See also the following reference:

J. H. Schulman and T. D. Smith, Selective Flotation of Metals and Minerals, Recent Developments in Mineral Dressing, *Inst. Min. and Met.*, 1953, p. 393, and other papers on theory and practice of flotation therein.

CHAPTER VI

MICROSCOPICAL (OPTICAL) EXAMINATION OF SEDIMENTARY ROCKS

Polarizing Microscope—Binocular Polarizing Microscope—Microscope for Particle Shape and Size Measurement Metallurgical Microscope—Magnification—Use and Care of Microscope—Accessories to Microscope Work—Universal Stage—Phase-Contrast Microscopy in Mineralogy and Petrology—Photomicrography—Systematic Examination of Sedimentary Rock Minerals under the Microscope Diagnosis of Minerals by Refractive Index (Immersion) Method—Summary of Optical Properties of Sedimentary Rock Minerals—Difficulties in Identification of Detrital Mineral Aggregates under the Microscope—Use of Coloured Light in Petrographic Work—Minerals Masked by Alteration Products.

POLARIZING MICROSCOPE

OPINIONS differ more on the most suitable microscope for petrographic work than on any other piece of apparatus designed for optical analyses of sedimentary rocks and minerals. For this reason no useful purpose is served in recommending any special type of instrument for the work described in this textbook. On the other hand, whatever make or version of microscope selected, it must at least be a polarizing design and embody certain essential basic equipment which the author has found indispensable to his own work.

Pl. 8 illustrates such a microscope suitable for all routine work and research projects concerned not only with petrology of sedimentary rocks but with many other applied sciences wherein technique of polarized light diagnosis has rapidly developed in recent years, *e.g.* biology, chemistry, ceramics and refractories, metallurgy, etc. Essential components are labelled so that the student should have no difficulty in recognizing vital parts concerned. In annotations that follow, function and use of each component are summarized. It is of utmost importance that before any serious work is begun, the microscope should be thoroughly mastered,

its potentialities appreciated and every possible adjustment familiarized. This statement may appear elementary, but it is remarkable how many difficulties in diagnosis of minerals or in optical determinations imagined by students can be explained by inability to use the instrument to full extent of its powers. In cases where practical instruction is not directly available, manufacturers' catalogues of polarizing and other purpose microscopes and accessories, usually afford abundant, detailed information on any particular model they supply and should be carefully studied. References quoted below will be found valuable expositions of principle and practice in the fundamentals of polarizing microscope design and optical physics¹. Here then are comments for guidance of novices.

BASIC STAND. This must be as rigid as a permanent optical bench. At any position, vertical to horizontal, that the instrument may be orientated, that rigidity must be firmly maintained. The stand normally embodies coarse and fine adjustments for motions of body-tube; bracket support for fixed or rotating stage; locking device to fix body-tube in desired working position; control mechanism for substage condenser; and mirror, double acting, plane and concave on reverse.

In the following notes, it is convenient to comment on components of a polarizing microscope (Pl. 5) from 'top to toe'.

EYEPIECE OR OCULAR. Function is to magnify near to the eye the image produced by the particular objective employed. The eyepiece reference graticule, now usually ruled on glass, N.-S., E.-W., intersecting 'cross-wires' or 'cross-lines' as they used to be called, is a standard fitting within the eyepiece in most microscopes used for petrological purposes. The intersection point acts as locus of observation and measurement. Standard magnification of eyepiece is usually $\times 6$; other magnifications are available, but $\times 10$, $\times 15$, $\times 20$ and $\times 25$, combined with a limited range of objectives (*q.v.*), serve to cover approximate magnifications from $\times 8$ to $\times 1300$ and more, quite sufficient for all ordinary work on sediments (this assumes standard tube-length of 160 mm.). Multiplication of eyepiece magnification by objective number (*q.v.*) gives approximate overall magnification of the instrument in use.

BODY-TUBE Normally 35 mm. diameter, 160 mm. tube-length. Carries eyetube for 30 mm. diameter eyepieces, with slot cut at 45° to cross-wires for insertion of quartz wedge, gypsum or mica plates, eyepiece

¹ A. F. Hallimond, *Manual of the Polarizing Microscope*, 2nd ed., (Cooke, Troughton and Sims, York, England), 1953.

N. H. Hartshorn and A. Stuart, *Crystals and the Polarizing Microscope*, 2nd ed., (Arnold, London), 1950.

A. F. Rogers and P. F. Kerr, *Optical Mineralogy*, 2nd ed., (McGraw-Hill, New York), 1942.

M. K. Wells (H. G. Smith), *Minerals and the Microscope*, 4th ed., (Murby, London), 1956.

A. N. Winchell and H. Winchell, *Elements of Optical Mineralogy*, 4th ed., (Wiley, New York), 1951.

micrometer graticules, etc. Sometimes incorporates upper Bertrand lens to slide in and out beneath eyepiece; in some older patterns this lens can be focused by moving an inner slide-tube containing it within a controlled vertical distance in the body-tube (20–25 mm.); modern instruments, however, incorporate an iris diaphragm mounted above Bertrand lens, to aid clear definition of interference figures, a great help with small detrital mineral grains.

The body carries towards its lower end an analyser, preferably sliding in and out of the tube; or this may be mounted over the ocular where fixed stage and rotating polar models are employed ('Dick' pattern). A lower Bertrand lens, push in and out type, is mounted immediately beneath the tube analyser; beneath this is the body-slot set at 45° to the N.-S. axis of the microscope, to permit insertion of quartz wedge and other compensators immediately above objective; this slot is protected from dust by revolving circular cover-band which closes the aperture when not in use.

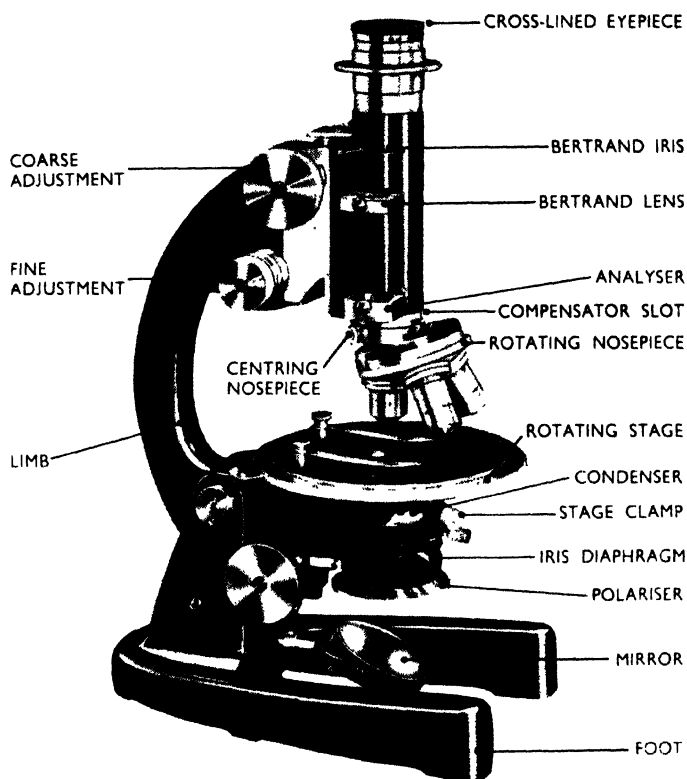
Immediately beneath the body-slot is set a centering mechanism (*infra*) for each objective used in single, double, triple or quadruple centering nose-piece mountings.

ANALYSER. Constructed of nicol prisms or nowadays more commonly of polaroid. When in body-tube vibration direction fixed (N.-S.) at right angles to vibration direction of polarizer.

CENTERING OBJECTIVES TO STAGE ROTATION. Most instruments are equipped with two centering screws to ensure that optical alignment of eyepiece, objective, and object under observation is correct. Where a rotating stage and double, triple or quadruple centering nosepieces are involved, as with petrological models, precise centering of each objective in use is a *sine qua non* to accurate work, especially when interpreting interference figures. There is nothing more annoying than to focus a mineral in thin section or detrital grain right on intersection of cross-lines with, say, a 1 in. objective and then, when increased magnification is desired for internal detail using, say, a $\frac{1}{4}$ in. objective, to find that the object has shifted away from intersection or even out of the field altogether.

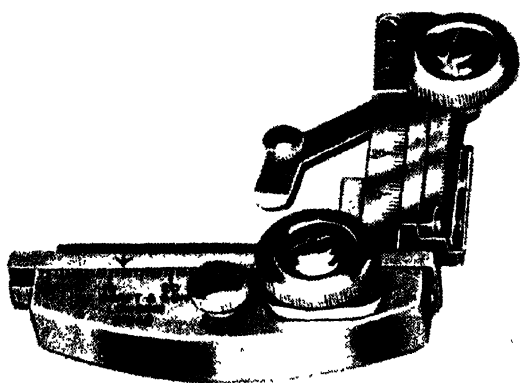
Centering screws are usually found immediately above the nosepiece and orientated at 45° each side of the N.-S. cross-line. If using a double, triple or quadruple nosepiece, centering should be perfect for highest magnifying power employed; then, if lower powers are brought into focus, even if the object is slightly off centre, it will not be 'lost' to view.

There is a modicum of skill involved in centering objectives, but once familiar with action of screws or other centering device for any particular instrument, the knack is soon acquired. The function of each screw turned separately is to cause the object to move in a definite direction; when combined, opposing directions gradually cancel and bring the fugitive mineral or grain back to dead centre. If the screws are carefully operated simultaneously, the process of centering is greatly facilitated. An air-bubble, if present in the slide, makes an admirable object for centering. Fig. 19 illustrates the function of centering screws and the

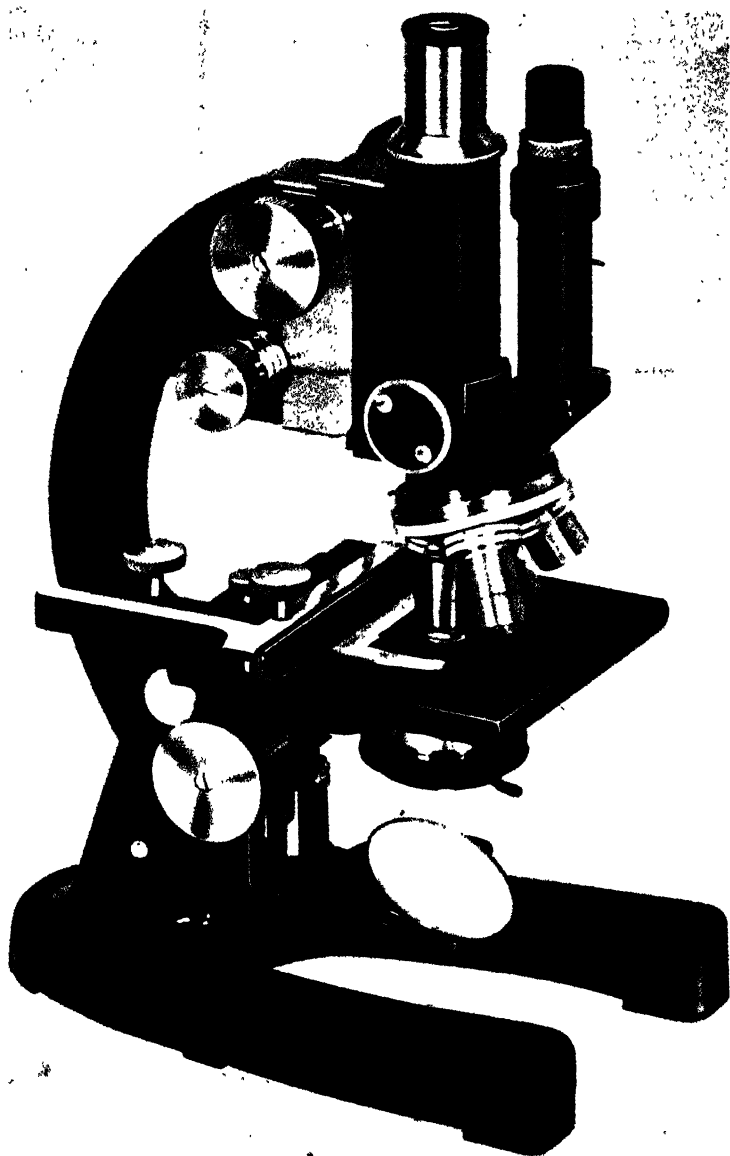


PETROLOGICAL MICROSCOPE.

(Courtesy M. K. Wells and F. Swift & Son Ltd., London, from H. G. Smith, Minerals and the Microscope, Murray, London, 4th ed. 1956)



ATTACHABLE MECHANICAL STAGE FOR ROUND STAGES
(Courtesy J. Swift and Son Ltd., London)



METALLURGICAL MICROSCOPE WITH ATTACHED INCIDENT ILLUMINATOR WITH
SELF-CONTAINED LIGHT-SOURCE
(Courtesy J. Smith and Son Ltd., London)

correction of location relative to cross-wires which, by proper manipulation, they are designed to bring about.

In some microscopes, especially foreign makes, centering changers are employed into which individual objectives are permanently mounted and slid into position as required in a tube fitting screwed on to the body, thus obviating use of rotating nosepieces. Advantage of changers is that once each objective is centered in its holder and locked, repeated centering for different objectives is avoided, except for occasional check-up.

NOSEPIECES. The polarizing microscope is normally fitted with a centering nosepiece or rotating nosepieces capable of accommodating two, three or four objectives at choice. This device permits of rapid changing from one power to another. Objectives should be inserted in the turrets of nosepiece in order of increasing magnification when it is rotated clockwise.

OBJECTIVES. For normal routine petrographic work, 1 in., $\frac{3}{4}$ in., $\frac{1}{2}$ in. and $\frac{1}{4}$ in. objectives are those most commonly employed. To this series a $\frac{1}{2}$ th. oil immersion can be added with advantage. Short mounts of higher powers, where practicable, are often useful. Standard achromatic objectives (45 mm. and less) available for polarizing microscopes of all well-known makes, are tabulated below¹.

TABLE 2. ACHROMATIC OBJECTIVES

Nominal Focal Length		Numerical Aperture	Initial Magnification	Working Distance
mm.	in.	N.A.	\times	mm.
45	2	0.12	3	45
45	2	0.17	3	34
32	1 $\frac{1}{2}$	0.12	4	32
32	1 $\frac{1}{2}$	0.20	4	18
25	1	0.16	5	26
25	1	0.25	6.5	13
16	$\frac{3}{4}$	0.17	10	14
16	$\frac{3}{4}$	0.30	10	7.5
12	$\frac{1}{2}$	0.50	14	1.55
6	$\frac{1}{4}$	0.80	30	0.58*
4	$\frac{1}{4}$	0.72	40	0.61*
4	$\frac{1}{4}$	0.85	45	0.41*
3	$\frac{1}{4}$	0.90	55	0.30*
3	$\frac{1}{4}$	0.92	60	0.23†*
2	$\frac{1}{4}$	1.2	90	0.18†*
2	$\frac{1}{4}$	1.3	90	0.18†*

* Can be supplied in short mount and computed for uncovered objects.

† Oil-immersion objectives.

¹ J. Swift and Son Ltd., London.

STAGE (ORDINARY). There are two kinds of non-mechanical stages fitted to polarizing microscopes for petrological purposes, either fixed rectangular (in models with rotating polars, e.g. 'Dick') or rotating plain round (the more usual version). In both types there is a central circular hole of at least 23 mm. diameter to permit free passage of transmitted light with or without substage system (*q.v.*); microscope slides or unmounted specimens of suitable dimensions are held in place by spring clips for retention during observation. Rotating stages should be fully graduated in degrees (0-360) and a tangential vernier reading to 0.1 degree fitted to the stage support, usually a little to the right of the limb of the stand. In modern instruments the centre (70 mm. diameter) of the rotating plain stage is removable to take care of rotation of the circle of a universal stage (if employed). In both circular and

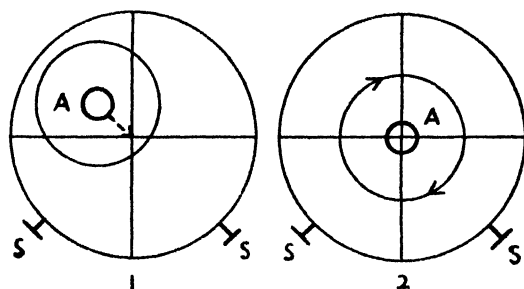


FIG. 19. Centering Objective. 1 Eccentric, 2 Centered. S Centering screws. A Air-bubble or mineral grain.

rectangular stages, tappings should be provided for spring clips, mechanical stages and other special accessories. The chief function of a graduated rotating stage in petrographic work is measurement of extinction angles of non-isotropic minerals and other optical characteristics searched in their diagnosis.

STAGE (COMPOUND AND MECHANICAL). What is known as the 'round compound (centering or non-centering)' stage is embodied in some microscopes where preferred. It is much the same as the ordinary rotating stage, except movements similar to those achieved by attachable mechanical stages are 'built in'. A lateral traverse of a 3 in. x 1 in. microscope slide up to 55 mm., and its transverse movement up to 25 mm., is practicable with this compound stage, the slide or specimen being held in place by spring clips.

For all ordinary routine work, however, the author much prefers the attachable (hence detachable at will) mechanical stage for round or fixed rectangular stages. In the former case the attachment should be so constructed that it can permit full rotation (through 360°) of the round stage without fouling objectives. It is bedded down to the stage by two dowel pins which fit into the ordinary spring-clip holes, and tightly secured by a central screw. In the pattern illustrated (Pl. 6)

both lateral and transverse traverses of standard 3 in. \times 1 in. microscope slides up to 25 mm. are practicable. Other models of attachable mechanical stages, suited to rectangular fixed stages of polarizing microscopes, are available with and without scales and verniers.

The primary function of any mechanical stage is to facilitate thorough, co-ordinated search of mounts of mineral grains or thin sections; counting different species present in any one mount or series of mounts; fixing positions of special minerals in slides by means of scales and verniers (so that given the same orientation of the slide, such special minerals may be quickly found again); generally to make movement of the object concerned orderly and without the relatively haphazard motions implicit in fingering the slide under spring clips.

SUBSTAGE SYSTEM. This normally comprises a swing-in and-out mechanism carrying a condenser mounted in an iris diaphragm, beneath which is located the polarizer, also capable of being swung in and out of the optic axis of the instrument. Substances may be of the plain sleeve, non-centering variety or preferably for precision optical work, fitted with centering condenser mount and subject to rack and pinion focusing.

CONDENSER. This is usually a two-lens system mounted in a metal sleeve fitted with iris diaphragm and swing-out, circular carrier for filters (coloured or plain), diffusing plates and patch-stops of varying design. The Abbe type is well known and is satisfactory for all normal petrological and mineralogical analyses. The function of the substage condenser is (a) to increase the resolving power of the objective, especially high powers, (b) to increase illumination, and (c) to enable optical measurements to be made, especially interpretation of interference figures.

IRIS DIAPHRAGM. This is an indispensable unit in the substage system. It is not only a part of the condenser set-up, but an additional one can also be fitted to the polarizer if desired. The function of iris diaphragms, wherever placed in polarizing microscopes, is to reduce the illuminated field of view and so concentrate on a particular mineral or grain or specific object under observation, that by increasing definition their diagnosis is thereby rendered easier. It is also of great assistance in delineating interference figures, by restricting peripheral spread of these sometimes diffused uniaxial or biaxial directions images (p. 237). Another use to which the iris diaphragm is conveniently put, is when it is required to mark on the cover slip a particular mineral or grain for photomicrographic work or future reference. If the object is centered in the light-circle with the diaphragm nearly closed, an ink-mark on the outer circle of light will pin-point it.

POLARIZER. Formerly constructed as a nicol prism, now generally a polaroid cell, it is mounted immediately beneath the condenser system and above the mirror. When in position, this cell polarizes all light transmitted from the mirror through the condenser to the object. The usual type of polarizer is graduated either at every 45° or 90° and

'clicks' at the zero position ('cross' position with analyser in body-tube or over eyepiece at correct orientation). Vibration direction of light transmitted through the polarizer is traditionally E.-W.

Note.—Polaroid is a synthetic, crystalline substance which in the comparatively thin circular discs cut for polarizing purposes is almost colourless. It has the property of absorbing one of the two vibration directions of light which passes through it, thus performing the function of the nicol prism in producing plane polarized light. Polaroid filters for polarizing microscopes must be free from pin-holes or other blemishes (*e.g.* striations); they should never reveal the slightest inherent birefringence; they should be as near colourless as possible. Polaroid discs are normally hermetically sealed between optical glass plates, especially important in the tropics. Polaroid filters should not be exposed to heat conditions above 140°F.

BINOCULAR POLARIZING MICROSCOPE

Many microscope manufacturers today standardize a basic stand in such a manner that interchangeable bodies can be substituted to meet biological, metallurgical, mineralogical or petrological requirements. The traditional biological research model, where a binocular body is nearly always standard fitment, can be adapted as a polarizing instrument; there are many occasions when, in petrographic work, this type of microscope is of high practical value.

The kind of specification required for such work is basic stand; inclined binocular body with one focusing eyetube and central interocular control; triple or quadruple nosepiece with adequate centering or individual centering changers; circular rotating graduated stage with vernier; condenser system embodying swing-out polarizer (p. 211). The analyser will be a non-rotating type fitted into the body-tube above the objective. Other accessories or facilities can be added to satisfy personal requirements in consultation with the manufacturer concerned.

In fully-equipped petrographic laboratories, the binocular *polarizing* microscope (or its parent 'stereoscopic' binocular microscope) is almost certain to find a place, because it is the complete answer to those engaged on intensive petrographic, especially micro-palaeontological, investigations in oilfields and elsewhere; apart from a measure of relief into which images are thrown with a binocular pattern, it also has a material advantage over the monocular instrument in lessening eye-fatigue sometimes occasioned by examination of many hundreds of microscope slides in succession. In this connexion some comments by M. I. Goldman some years ago, are still apposite¹.

As this instrument may at outset take a little more understanding

¹ *Bull. Amer. Assoc. Petrol. Geol.*, 9, 1925, p. 175.

than a monocular pattern, the following notes from the author's experience may help the student in its use:

(a) In investigating well-samples, large fragments of rock, micro-fossils, individual minerals and all opaque materials, dark-ground illumination if required may be secured by placing either a white or black card (depending on the colour of the substance examined) on the stage and employing strong incident light, preferably from an illuminator attached to the body-tube of the instrument (see p. 215).

(b) Everything depends on correct adjustment and intensity of illumination, whether transmitted or incident, a matter of much greater importance than with the simple-pattern microscope. If daylight available is not sufficiently strong, use a 100-watt gas-filled 'daylight' type electric lamp. With transmitted light, rays should fall directly on the concave mirror, care being taken to adjust so that filament is not reflected in the instrument. With incident light, allow rays to fall obliquely on to the object on the stage, unless special dark-ground illumination apparatus is employed, when this adjustment will be made automatically.

(c) A 1 in. objective normally suffices for all ordinary work with this instrument, but higher power ($\frac{1}{2}$ in. or $\frac{1}{4}$ in. in short mounts) can be used when the object is not too large, care being taken not to scratch the objective when racking down to focus. For examination of thin sections, transparent objects, detrital mineral grains mounted on glass slips, etc., with transmitted white light and 1 in. objective, the condenser is not always necessary and the polarizer should be swung out of the optic axis until it is required for polarized light determinations. Where the high-power objective is being used with transmitted light, it is essential to employ the condenser, otherwise the illumination may not be sufficiently strong, or may be partly cut off.

(d) Focusing is effected primarily by coarse adjustment, actually quite a sensitive mechanism, secondarily by fine adjustment and further by focusing eyetube.

(e) For interference figures in rock-minerals with this instrument, insert condenser, swing in polarizer, use high-power objective, push in analyser and remove both oculars: observation through either ocular-tube with the eye a little distance away from aperture and, if necessary, shifted slightly to right or left, will reveal the desired figure on a small scale. Alternatively, a Bertrand lens in the body-tube obviates necessity of removal of oculars. Determination of sign with quartz-wedge is carried out in normal manner by inserting it in slot at bottom of body-tube underneath analyser; the wedge is thus placed 45° to cross-wires; see p. 239.

(f) Should there be any trouble with nicol prisms owing to excessive heat (e.g. tropics), detach both polarizer and analyser and send them back to manufacturers. This possibility is, however, remote and can be largely avoided by keeping and using the instrument, or any microscope for that matter, in a cool room during this time. *On no account attempt*

to repair the prisms without expert advice. With polaroid nothing is likely to happen at temperatures below 140°F.

MICROSCOPE FOR PARTICLE SHAPE AND SIZE MEASUREMENT

When working on sediments or crushed rock powders of all descriptions, especially where check of results of mechanical analysis by microscopical means is desired, it is advantageous to employ an instrument specially designed for the purpose. One in constant use in the author's laboratories, which has proved invaluable in the course of particle size determinations, embodies the following features:

- (1) Standard horseshoe-type base, very rigid and firm, curved limb for easy lifting, 3 cm. diameter body-tube. The stand is steady in all positions, from vertical to horizontal, the latter important when projecting slides of particles on to a screen for measurement (p. 192).
- (2) Coarse and fine adjustment.
- (3) Rotating stage (with thumb-screw clamp for fixing if necessary) graduated in 360° with vernier reading to 5 minutes, fitted with clips (removable) to hold slide, also with sockets to receive special form of stage micrometer (p. 222).
- (4) Iris diaphragm carrying condenser.
- (5) Double mirror, one plane, the other concave for convergent light and high-power magnification.
- (6) Interchangeable oculars: (a) $\times 6$ with co-ordinate ruling, lines being 0.1 mm. apart; (b) $\times 6$ with ordinary eyepiece reference graticule; (c) $\times 20$ (12.5 mm.) for specially high-power work.
- (7) Objectives 1 in. (N.A. 0.25); $\frac{1}{2}$ in. (N.A. 0.50); $\frac{1}{3}$ in. (N.A. 0.80), $\frac{1}{4}$ in. (N.A. 0.85); $\frac{1}{5}$ in. oil immersion (N.A. 1.30).
- (8) Eye-piece and stage micrometers (p. 222).

METALLURGICAL MICROSCOPE

However much the ordinary petrological microscope is adapted by temporary ways and means to work with reflected, as distinct from transmitted, light there are nowadays so many 'incidents' in sedimentary mineral and rock diagnoses demanding a permanent, self-contained, reflected light instrument, available side by side, so to speak, with the standard petrological type, that the metallurgical microscope has become increasingly popular in this field. The type (Pl. 7) in constant use in the author's laboratories incorporates, apart from coarse and fine adjustments to the body, rack and pinion adjustment to the main stage; the latter has an aperture in case it is desired to use the instrument for examination of transparent objects

(with facilities to fit mirror and substage condenser). The most important feature, however, is that the illuminator is 'built-in' to the body furniture and permits the use of a rotating nosepiece accommodating up to four objectives, in short mounts where necessary. Reflected light is by means of a 6-volt bulb, connected to a.c. mains through an appropriate transformer. This illuminator unit includes condenser lens, two iris diaphragms and filter. It is also practicable to operate a mechanical stage on this instrument.

Differentiation of opaque minerals, especially iron ores, in heavy mineral residues, of compound mineral aggregates so often found in the finer sediments, of polished fragments of mineral, ore or slag (B.S.1047:1952), is rendered more quickly, by light contrast, with this microscope than with any other type.

MAGNIFICATION

Initial magnification of a microscope may be defined as the ratio of dimensions of the image formed in the focal plane of the eyepiece, to that of the object under scrutiny. Total magnification is the product of multiplying initial magnification of the objective by that of the eyepiece involved. Thus a 16 mm. ($\frac{2}{3}$ in.), N.A. 0.30, initial magnification $\times 10$ objective with a $\times 6$ eyepiece in 160 mm. body-tube, gives a total magnification of 60 (approximately). *If precise magnification is called for in any combination of eyepiece and objective, this must be measured by stage micrometer (p. 222) against a suitably ruled eyepiece micrometer (p. 220).*

'The numerical aperture . . . gives the measure of the resolving power of an objective, i.e. its ability to resolve the separation of two adjacent points of an object. The greater the numerical aperture, the greater the resolving power¹.' By increasing the power of the eyepiece, total magnification is automatically increased, but there is a theoretical limit to such increase in resolving the object under examination beyond which no practical advantage is gained.

'The so-called Maximum Useful Magnification that can be obtained from an objective is approximately 1,000 times its numerical aperture. Thus a 4 mm. ($\frac{1}{4}$ in.) objective of initial magnification $\times 45$ and N.A. 0.85 will give a Useful Magnification of $\times 850$, which could be approximately achieved with a $\times 20$ eyepiece ($45 \times 20 = 900$). With a $\times 25$ eyepiece, however, the total magnification would be 1,125, which is greatly in excess of the Maximum Useful Magnification. In general, the mineralogist is less concerned with resolution than the biologist, but the greater the N.A., the greater the angular coverage of the objective, and this factor is of great importance for the mineralogist when measuring the optic axial angles of crystals from their interference figures².'

^{1, 2} *Objectives—General Information*, J. Swift and Son Ltd., London, 1956.

In the following table approximate magnifications are given in terms of nominal focal lengths, numerical apertures and initial magnifications of objectives, with different eyepieces, assuming body-tube length of 160 mm., image distance 250 mm. (usual standard tube). If body-tube is longer or shorter in length than 160 mm., magnification will be given by multiplying the magnification figures in the table by the number of mm. increase or decrease in tube-length and dividing the result by 160.

TABLE 3. APPROXIMATE TOTAL MAGNIFICATIONS¹

Nominal Focal Length ² mm. in.	Numerical Aperture (N.A.) ³	Initial Magnification ⁴	Tube Length 160 mm. Image Distance 250 mm. ⁵							
			Eyepieces							
			×4	×6	×8	×10	×12	×15	×20	×25
75 3	0.08	×1.5	6	9	12	15	18	23	30	33
45 2	0.17	×3	12	18	24	30	36	45	60	75
32 1½	0.20	×4	16	24	32	40	48	60	80	100
25 1	0.25	×6.5	26	39	52	65	78	98	130	158
16 ¾	0.30	×10	40	60	80	100	120	150	200	250
12 ½	0.50	×14	56	84	112	140	168	210	280	350
6 ¼	0.80	×30	120	180	240	300	360	450	600	750
4 ⅙	0.85	×45	180	270	360	450	540	675	900	1125†
3 ⅓	0.90	×55	220	330	440	550	660	725	1100†	1375†
3* ⅔	0.92	×60	240	360	480	600	720	900	1200†	1500†
2* ⅓	1.3	×90	360	540	720	900	1080	1350	1800†	2250†

* Oil immersion objectives.

† Value beyond limit of Maximum Useful Magnification (see p. 215).

Notes

¹ The magnifications given in the above table are based on the range of objectives and eyepieces manufactured by J. Swift and Son, Ltd., London; they approximate reasonably values for objectives of similar focal length but of different N.A., as well as for comparable objectives and eyepieces produced by other makers.

² In older patterns, British objectives were often engraved with focal length in in., foreign in mm. Modern British objectives now usually bear focal length in mm., N.A. and initial magnification numbers (see Table 2, p. 209).

³ For explanation, see p. 215.

⁴ See Table 2, p. 209.

⁵ The 160 mm. tube-length is a standard fitment except for inclined monocular and binocular bodies when the tube-length is increased. A suitable correcting lens is provided in such cases to compensate and preserve original computations for initial magnifications of objectives as given (p. 209).

USE AND CARE OF MICROSCOPE

The microscope is a very 'long-lived' instrument if treated with care and respect. It survives handling (sometimes mishandling) by successive generations of students to a remarkable degree, often with comparatively little maintenance. Short of accident, return to manufacturers for overhaul is exception rather than rule, although it has always been the author's custom to advise this policy from time to time, for check-up and additional accessories as may be required.

IN USE, the following points should be noted, assuming the set-up of the instrument is ready for working:

(a) The best working position for physical comfort with monocular patterns is about 60° from vertical.

(b) Accustom yourself to work with both eyes open, the right eye being used for observation through the instrument. Those who normally wear spectacles should if possible keep them on during observations. With bifocal lenses adjustments may have to be made, for instance, the near-reading lenses may have to be replaced by spectacles containing only single reading lenses, if complete comfort is to be maintained.

(c) With daylight illumination avoid direct sunlight. A north-facing light is best. Avoid all reflections, *e.g.* window-frames or external objects.

(d) With artificial illumination use a microscope lamp specially designed for the purpose. In other circumstances, simple pearl or opal ordinary or 'daylight' type lamps may be employed suitably mounted and orientated. Avoid unobscured electric light bulbs.

(e) Use concave side of mirror for ordinary routine work with low-power objectives; the plane mirror must be used with the condenser system.

(f) Using objectives with initial magnifications up to $\times 10$ (16 mm. or $\frac{5}{8}$ in.), the condenser can be dispensed with in routine work. Above that magnification the condenser is indispensable. See that it is correctly focused and centered.

(g) Make full use of the iris diaphragms provided. It is astonishing how many students engaged on routine work seem to ignore these aids to diagnosis, especially when working with convergent light; the quality of the image, especially directions images, depends primarily on perfectly balanced illumination and the iris diaphragm is there for that purpose.

(h) With oil-immersion objectives, a drop of cedarwood oil must be placed on the cover glass or object under observation and the front lens be immersed in this drop. Do not overdo the oil. Wash oil clean of objective after use with fine linen rag which may be moistened with xylol to assist removal. Never use alcohol or methylated spirits for this purpose.

for light filters. Both height and inclination are easily adjustable. It is of universal use, with low- and high-power work, dark ground illumination and especially in photomicrography.

The second type (Fig. 21), in which light from an electric bulb is made to pass through a cylindrical, clear glass rod ('speculum'), has the advantage that the illuminant has uniform intensity and is circular in shape, the former being alterable within wide limits without change of quality. This form of lamp has been developed by F. Welch and is fully described¹. It is especially suitable for routine microscopical work with artificial transmitted light where daylight is inadequate.

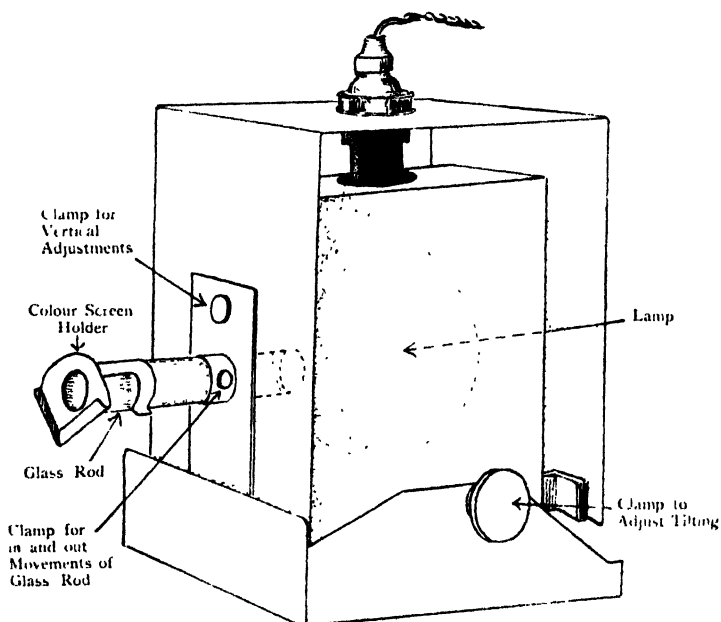


FIG. 21. Microscope Lamp. (After F. Welch, *Journ. Roy. Microsc. Soc.*, 50, 1930, p. 34-37.)

Provision for monochromatic light may be made by the simple method of suspending a bead of sodium salt in a platinum wire loop held in a bunsen burner. A more scientific method is to employ a lamp in which a glow discharge takes place in sodium vapour,

¹ *Journ. Roy. Microsc. Soc.*, 50, 1930, p. 34.

such a lamp being coupled to a suitable rectifier to supply heating current to the filament¹.

Dark Ground Illumination. Observations of objects by reflected as distinct from transmitted light depend on the principle that light-rays are scattered from the surface of the object (if opaque) or from the interior if transparent or translucent, without passing through the objective. This principle is well illustrated by the metal-lurgical microscope described on p. 214. There are, however, other means of securing dark ground illumination, (a) by means of patch-stops emplaced in the substage system (a certain amount of transmitted light gets past these); (b) with the intensity lamp previously described (p. 218); (c) with specially designed dark ground condenser. The latter is a most efficient but somewhat complicated system of dark ground illumination, requiring the use of immersion oil as medium between condenser lens and microscope slide or object to be studied. Full details of operation with this type of condenser are given by the makers².

Another, simple form of dark ground illumination is illustrated in Fig. 22. This consists of a small $3\frac{1}{2}$ volt lamp and aplanatic condenser, carried in a tube easily attachable to the nose of the microscope. It permits accurate control of top lighting for all routine purposes.

Eye-Piece Micrometer Graticules. There are several types of graticule now available for particle size or object measurement under the microscope. The standard mounting is on a 21 mm. glass disc which is itself mounted in a metal or vulcanite cell 28 mm. diameter for insertion in the eyepiece. Alternatively the graticule may be a smaller glass disc, 14 mm. diameter and mounted in rectangular holder 50 mm. \times 20 mm. for insertion in the slotted eyepiece. In point of fact glass discs can be supplied ground to any desired size less than 21 mm. and the same applies, within limits, to dimensions of rectangular carriers.

Micrometer graticules recommended for normal routine work on mineral grains are as follows:

10 mm. in 100 parts horizontal numbering 1-10.

10 mm. in 100 parts vertical numbering 1-10.

10 mm. in 100 parts horizontal and vertical crossed scales 1-10.

Eyepiece squared graticule, squares of side 0.5 mm. every tenth line thickened.

0.1 in. in 100 parts horizontal numbering 1-10.

¹ Phillips Industrial, London.

² *Dark Ground Illumination*, J. Swift and Son Ltd., London, 1956.

Perhaps the most commonly used graticule in work on sedimentary rock particles is the 10 mm. in 100 parts horizontal numbering 1-10 mounted in metal carrier, so that the scale reads parallel to the carrier when placed in slotted eyepiece at 45° to the N.-S. axis of the microscope. This graticule is valuable for certain measurements of directions images apart from particle size determinations.

Apart from those above described, there are also available some special forms of eyepiece counting and particle sizing graticules such as the Patterson and Cawood Globe and Circle¹; the Porton Graticule (a modified form of the Patterson and Cawood design); Fairs Graticules Nos. 1, 2 and 3²; the Simplified Globe and Circle Pattern (National Coal Board)³; V-Scales ('Athene')⁴; Circular Graticules (concentric circles of diameter 0.5-12 mm. in 0.5 mm. steps or in $\frac{1}{64}$ in.- $\frac{3}{8}$ in. in $\frac{1}{64}$ in. steps); and Angular Graticules (protractor semicircle, 0-180° with base scale of 10 mm. divided into 0.5 mm.). Most of these eyepiece graticules are figured and described⁵.

In making measurements with eyepiece micrometer graticules, some initial calibration is necessary because divisions on the scales are arbitrary and their value alters with change of magnification. It must be remembered that any calibration made is only true for a known combination of eyepiece, micrometer graticule and objective. Procedure is to insert the particular eyepiece graticule selected and calibrate against a standard stage micrometer. Lines on both the former and latter are focused together and then the stage micrometer is shifted until specific lines on both eyepiece and stage micrometers are coincident. Ratio of the number of divisions on the eyepiece scale relative to those on the stage micrometer scale is the absolute measurement of the eyepiece divisions. Thus, if 60 divisions on the eyepiece scale coincide with 0.3 mm. on the stage micrometer scale, then each division of the eyepiece scale is 0.3 divided by 60 which equals 0.005 mm. The combination of $\times 6$ eyepiece, 10 mm.

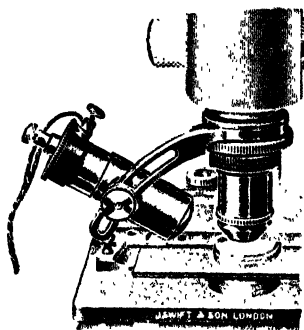


FIG. 22. Dark Ground Illuminator.

¹ *Bull. Inst. Min. Met.* 386, 1936.

² G. L. Fairs, *Chem. and Ind.*, 62, 1943, No. 40, p. 374

³ H. H. Watson, *Brit. Journ. Ind. Med.*, 9, 1952, p. 80.

⁴ Smethurst Heat-Light Ltd.

⁵ *Graticules*, J. Swift and Son Ltd., London, 1956.

in 100 parts horizontal numbering 1-10 graticule, 160 mm. standard body-tube and 25 mm. (1 in.), N.A. 0.25 objective, and standard stage micrometer (as described below) is a convenient set up for calibrations of this nature. From specific eyepiece calibration and known magnifications in use, actual size of a particle under observation is readily determined.

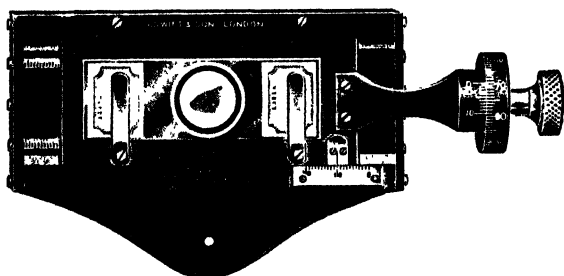


FIG. 23. Auxiliary Stage Micrometer.

In the type of microscope described on p. 214, one of these in use in the author's laboratories has a squared graticule permanently fixed in the eyepiece, with stage micrometer attached to rotating stage. Using this graticule in $\times 6$ ocular, 160 mm. body-tube and 12 mm. ($\frac{1}{2}$ in.) objective, each side of a square represents approximately 30μ ; with a 4 mm. ($\frac{1}{6}$ in.) objective, each side represents 10μ . These are just two examples of permanent calibration of an eyepiece graticule enabling individual particle size and grain-size ranges to be accurately and rapidly established. Micron measurements, below 10μ down to 1μ , can be estimated with a considerable degree of accuracy with this outfit.

Stage Micrometer. A special form of auxiliary stage micrometer was constructed at the author's suggestion some years ago by J. Swift and Son, Ltd., London, embodying the principles of expeditious and accurate measurement of particle size to 0.001 mm. It can be employed on any microscope irrespective of body-tube length, ocular or objective used, and will be found invaluable in all determinations associated with mechanical analysis (Fig. 23).

The apparatus, which is placed upon the stage of the microscope, consists of a supplementary stage, which is moved in a dovetailed slide by a micrometer screw of 1 mm. pitch. This screw carries a drum with one hundred divisions, each the equivalent of 0.01 mm. of the object; these divisions, in their turn, are sub-divided by means of a vernier to

0.001 mm. The range of the screw is 20 mm., so objects up to this size can be measured; complete revolutions of the screw, each 1 mm., are recorded on a scale on the edge. Measurement is made against a line or web in the ocular.

In use, the slide bearing the object to be measured is placed on the micrometer stage and focused in the ordinary manner. By means of the screw, one edge of the particle to be measured is brought against the web or line in the ocular and the reading of the scale and drum noted; the movement is then continued until the other edge is coincident with the web, when the difference between the reading of this position and the first gives the actual length of the object.

The usual and most satisfactory manner of attaching this micrometer stage to the microscope is by means of a small knurled head with a standard 6 B.A. thread, which screws into a tapped hole in the main stage; several models of Swift microscopes are provided with this tapped hole as standard practice. . . . Instead of this method it may be held sufficiently rigidly on the main stage by means of small pellets of 'Sira' wax or plasticine, to accommodate which there are four small recesses on its under side; for this purpose a small ball of wax, slightly more than enough to fill it, should be pressed into each recess, the micrometer placed in the correct position on the main stage and the two then firmly pressed together.

The use of a co-ordinate ruling in the ocular in conjunction with the micrometer stage still further facilitates measurements of average particle size. A very convenient ruling is one which gives squares of approximately 0.01 mm. side when used with a $\frac{1}{4}$ in. objective on a standard length body-tube. The ruling is calibrated with the micrometer stage and measurements are carried out by estimating the area covered by the particle in squares and fractions of squares. Fresh particles may be brought into the field by turning the screw of the stage¹.

Other accessories under this heading are Stage Micrometer Scales, which are ruled on standard 3 in. \times 1 in. glass slips, the ruled part being protected by suitable cover glass. The usual ruling is 10 mm. to 0.1 mm. but other rulings are available, e.g. 0.1 in. to 0.01 in. or 0.001 in.

Spectroscope for Petrological Microscope. A simple form of spectroscopic attachment (Fig. 24) may be usefully employed with a petrological microscope in which a slotted eyepiece is available, when examining concentrates for rare-earth minerals, e.g. monazite. This consists of a prism *A* mounted to fit over the ocular and a brass plate *B* for insertion in the slot. The plate is provided with an adjustable slit, variable in length by a slide having a V cut at one end. The width of the slit can be controlled by means of a thumb-screw at the right end of the plate.

¹ From notes accompanying the micrometer.

Compensators. For precise optical work a mica or gypsum plate and a quartz wedge are essential. The mica plate, sometimes known as a 'quarter-wave plate', is made in such a way that retardation of one of the two rays into which it splits the light is $\frac{1}{4}$ -wavelength behind the other. The mica is cut in the form of a rectangle, the edges of which are parallel to the two directions of vibration and suitably mounted on a glass slide, usually half the width of the ordinary 3 in. \times 1 in. slip.

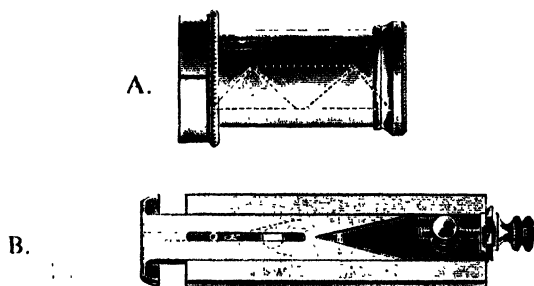


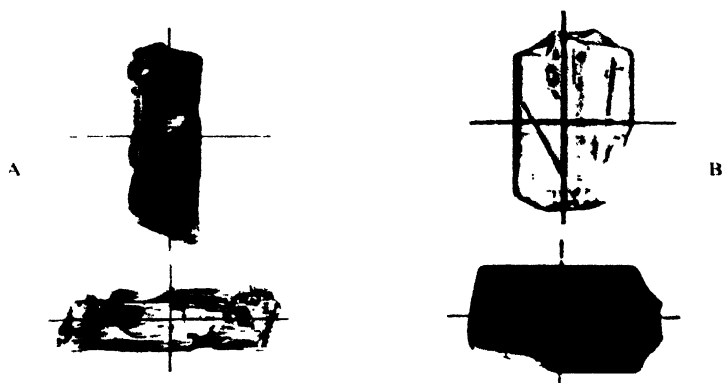
FIG. 24. Spectroscopic Eyepiece Attachment.

A. Prism to fit over ocular of microscope.

B. Brass plate with adjustable slit for insertion in slot.

The gypsum or selenite plate, sometimes known as a 'unit retardation plate', is cut in a similar way from a well cleaved, flawless crystal. The 'cleavage flake' is chosen which gives 1st order red; this is suitably cut and mounted as in the case of the mica plate and used to produce a retardation of one wave length.

The quartz wedge is constructed from specially selected quartz crystal ground down parallel to the crystallographic *c*-axis or optic axis, in the form of a wedge, one end being as thin as possible, the other of a thickness which ensures that at least five 'orders' of colour are shown by the whole wedge when viewed between cross nicols. These colours take the form of bands traversing the wedge at right angles to its length, each band corresponding to different degrees of retardation of the light as it is transmitted through different thicknesses of the quartz unit. Such a wedge is best calibrated along its length at appropriate places to denote relative retardation (in $\mu\mu$) and order limits. It is normally mounted in a similar manner to that of the mica or gypsum plate; as thus supplied, its length coincides with the slow direction (ϵ) of light vibration and this is frequently indicated by an arrow engraved on

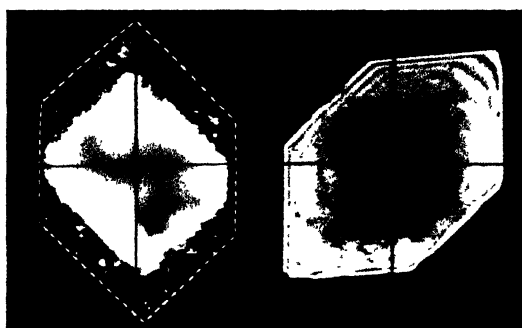


A, B PLEOCHROISM.

TOURMALINE.

DUMORTIERITE.

N.B. - Vibration direction of polariser E-W.



C. PARALLEL EXTINCTION.

Quartz 90 position 45 position

Note - Outgrowth *not* in optical continuity with nucleus.



D. OBLIQUE OR INCLINED EXTINCTION. Kyanite 90 position. 45 position

the wedge parallel to its length, followed by the letter ϵ (Fig. 25).

An alternative to this convention is the J. W. Evans double quartz wedge which consists essentially of two wedges mounted side by side, but so ground that one exhibits the slow direction (ϵ), the other the fast (ω) in parallel position on the mount. Such a wedge shows simultaneously the effect of insertion at 45° in two directions.

The Klein plate, which is not often employed in petrological work, where nicol prisms are properly calibrated, is a means of determining accurately that the polarizer and analyser are properly crossed with maximum darkness ensuing. It consists of a section of specially selected quartz crystal cut at right angles to the crystallographic c -axis or optic axis and of the necessary thickness to give a violet tint; this colour changes perceptibly with the slightest rotation of either or both of the nicol prisms.

Babinet Compensator. This is a most sensitive instrument, a refinement for advanced studies in optical physics. Its function is to determine characteristics of elliptically polarised light, *e.g.* phase difference, axial ratios and positions, birefringence in transparent media, etc.

The model described here 'consists of a Ramsden eyepiece which is mounted above two acute quartz prisms, or wedges, having equal angles of approximately $2\frac{1}{2}$ degrees. The upper wedge, 11 mm. \times 11 mm., remains fixed in the body of the eyepiece, and the lower, 11 mm. \times 42 mm., can be moved by means of a calibrated micrometer screw of 0.5 mm. pitch. The screw is fitted with a divided drum, each division of which corresponds to 0.01 mm. The vibration directions of the two wedges are at right angles to each other, and the fixed wedge is provided

APPROXIMATE COLOUR	MM. O	ORDER
DARK GREY	100	1st
PALE GREY	200	
CLEAR YELLOW	300	
BROWNISH YELLOW	400	
REDDISH ORANGE	500	2nd
INDIGO	600	
BLUISH-GREEN	700	
PALE GREEN	800	
YELLOW	900	3rd
ORANGE RED	1000	
DARK VIOLET RED	1100	
BLUE	1200	
YELLOWISH-GREEN	1300	4th
PALE GREEN	1400	
PINK	1500	
MAUVE	1600	
PINK	1700	5th
PALE GREEN	1800	
GREEN	1900	
GREENISH YELLOW	2000	
PINK	2100	6th / 1st
PALE MAUVE	2200	
PALE GREEN	2300	
PALE GREENS AND OR WHISK PINKS	—	

FIG. 25. Polarization Colour Scale and Quartz Wedge as viewed between crossed nicols at 45° to N.-S. direction.

with fine datum webs which form a cross whose intersection lies on the optical axis of the instrument. . . . The analyser is of Polaroid, mounted between optically-worked glass plates in a sleeve which fits above the Ramsden eyepiece.

'The instrument is inserted in the eyetube of the microscope, in place of the usual eyepiece, and is set by means of a locating pin, or clamp, until the axes of the quartz wedges are at 45° to the E.-W. vibration direction of the polarizer of the microscope. The micrometer drum is then set to the zero position and the analyser placed above the eyepiece in the crossed position to the polarizer. If the illuminant is white light a black line appears in the centre of the field and coloured bars of light on either side. If monochromatic light is used, such as from a sodium lamp, black bars or fringes will appear on either side of the centre position. The fringes appear where compensation occurs of the two rays passing from the lower wedge, and they are separated by spaces which have the colour of the monochromatic light; in the case of sodium, this would be yellow. The angles of the wedges are such as to give fringes about 0.7 mm. apart, and the field of the Ramsden eyepiece embraces about 6-7 fringes.

'The distance between two black compensation bars is the wavelength of the illuminant, and the micrometer drum and scale are calibrated by observing the movement necessary to move the wedge from fringe to fringe. The constant of any instrument, using sodium light, is then found by:

$$K = \frac{589 \text{ millimicrons}}{\text{Drum divisions}}$$

'When a mineral specimen is placed upon the stage of the microscope and turned 45° from the position of extinction, the dark bar in the centre of the compensator will be displaced to the right or left, depending on its vibration direction. The amount by which the micrometer drum must be turned in order to return the black bar to the intersection of the cross-webs represents the retardation (in millimicrons, from the calibration) of the light that has passed through the mineral specimen. The retardation of a birefringent mineral is given by:

$$R = M(n_2 - n_1)$$

where M is the thickness of the specimen, and n_2 and n_1 the refractive indices in the two vibration directions at right angles to each other.

'The birefringence of a specimen can thus be determined if its thickness is known, and the latter can be determined by micrometer measurement, or if this is not practicable, by focusing on upper and lower surfaces of the specimen using the calibrated fine adjustment control of the microscope¹.

UNIVERSAL STAGE

Otherwise known as the Federov or theodolite stage, this constitutes a method by which certain fundamental optical properties of crystals, detrital minerals and minerals in thin section can be

¹ *Babinet Compensator*, J. Swift and Son, Ltd., London, 1956.

explored and accurately determined in a manner denied to the ordinary polarizing microscope. This type of stage provides a means of rotating the object on four or five axes in such a way that it is made to assume different orientations but without displacing it from field-centre. It is thus a precision system of the greatest possible value in advanced crystallographical, mineralogical and petrological work, especially in cases where such functions as optical orientation, optical sign, optic axial angle, pleochroism, dispersion, refractive indices, etc., are to be accurately measured. The universal stage is not only an auxiliary to optical investigation of identified crystals; it can be also a useful tool in differentiating optically between unidentified, although may be suspected species, leading to positive diagnosis. Another use to which it may be put is in analysing statistically component mineral orientations in certain types of sedimentary, but predominantly igneous rocks.

The essential features of design of a *four-axis* universal stage are:

(a) where polarizing microscopes contain a movable central disc in rotating stage, the universal stage can be securely mounted on existing stage of instrument;

(b) four axes of rotation of stage, inner vertical axis, north-south axis, outer vertical axis, E.-W. axis; inner and outer vertical axes are parallel to body-tube of microscope; N.-S. and E.-W. axes perpendicular to each other in horizontal plane of stage at rest position;

(c) axial rotations individually controlled by arresting screws;

(d) movements on N.-S. axis measured by graduated vertical arcs and circle, on inner vertical and E.-W. axes by graduated circles;

(e) graduated drum located on side of stage as mounted, permitting rotation of stage about E.-W. axis;

(f) glass disc fitted to central part of stage;

(g) glass hemispheres of different refractive indices supplied with the equipment.

Practical instruction and a good deal of experience are necessary to efficient working with the universal stage; a background knowledge of optical physics is imperative.

Details of set-up of objects under investigation and of manipulation of the universal stage are to be found in most textbooks on polarizing microscopes. Some references below are recommended to those who desire to follow up both theory and practice with this versatile instrument¹.

¹ J. C. Haff, Federov (Universal-Stage) Method of Indicatrix Orientation, *Quant. Colorado Sch. Mines*, 37, 1942, p. 1.

A. F. Hallimond, *Manual of the Polarizing Microscope*, (Cooke, Troughton and Sims, Ltd., York, England), 1953, Ch. 17.

A. F. Hallimond and E. W. Taylor, *Mineral. Mag.*, 29, 1950, pp. 150-162, (for the 3-axis universal stage).

I. F. Wahlstrom, *Petrographic Mineralogy*, (Wiley, New York), 1955, Ch. 4.

PHASE-CONTRAST MICROSCOPY IN MINERALOGY AND
PETROLOGY

The principle of phase microscopy, hence underlying the phase microscope itself, is contained in the fact that when light is transmitted through an object it follows an optical direction which is influenced both by refractive index and thickness of that object. Variations in both these properties combine to produce differences, sometimes quite small, in paths of light transmitted. Now differences in refractive index of many substances, including minerals, are often invisible with the ordinary microscope, owing to high intensity of light transmitted, but such differences, if suitably exploited, can be of great diagnostic value, as was discovered some years ago in biological research.

In its simplified form, phase-contrast microscopy can be made use of by converting the ordinary microscope with the addition of two essential accessories, an annulus to fit in the substage condenser system and a phase or diffraction plate in the objective; the former produces a restricted cone of light transmitted to the object, the latter has the effect of increasing the phase difference of the light rays.

What happens is that some of these guided light rays pass through the object with little or no deviation; other rays deviate to an extent dependent on refractive index variation in the object; in other words, such rays travel farther than the 'fixed path' rays and they are thus out of phase. The diffraction plate increases phase difference to a maximum and at the same time rectifies the intensity of both sets of light rays as they penetrate the object. Thus the image actually seen in the phase contrast microscope reveals the effect of differences in refractive index of the object which would not be disclosed with the ordinary brightfield microscope; such differences are, as stated above, of definite diagnostic value, especially with certain minerals, as has been shown by F. Smithson¹.

He states: 'In thin sections, the structures of rocks containing colourless minerals of similar refractive indices (for example, quartz and the feldspars) showed up very clearly with phase contrast; in these cases a further improvement in the image sometimes resulted from the use of a single "Polaroid" filter placed in the beam. In Canada balsam mounts of China clays, the shapes of the larger particles were very clearly seen . . . the technique represents a development which the mineralogist ought not to neglect. The phase-contrast equipment used . . . consisted of a special condenser

¹ Phase-Contrast Microscopy for Mineralogy, *Nature*, 158, 1946, p. 621. Also The Application of Phase-Contrast Microscopy to Mineralogy and Petrology, *Miner. Mag.*, 28, 1948, p. 384.

with annular diaphragms and a set of four objectives, giving magnifications of 10, 20, 40 and 95, each with its integral phase plate.'

'Smithson points out that path differences arising from differences in thickness, differences in compensation, and, with polarized light, differences of refractive index arising from optical orientation are made visible with the phase microscope; but it may be difficult to determine which are involved, especially when roughness of the specimen is also part of the problem¹.'

There is no doubt that, especially with the difficult clay minerals, phase microscopy is a powerful weapon in the hands of those fortunate petrologists to whom the more abstruse problems in optical physics are almost second nature.

PHOTOMICROGRAPHY

Although this subject is not strictly within the scope of a treatise on sedimentary petrography, in view of the prominent part that both photomicrographic apparatus and highly skilled photomicrographers have taken in production of so many of the beautiful illustrations of detrital minerals and sedimentary rocks in this book (especially Volume II), a brief description of what is involved, together with appropriate references to relevant authorities, may prove of use to those petrologists with photographic bent and who desire to record in permanent manner, some of their better observations under the petrological microscope.

The monocular polarizing, metallurgical and size-measuring instruments previously described in this chapter are all suitable for photomicrographic work; the microscope selected for the purpose in view is, of course, the most important unit in the set up of apparatus required, the latter consisting essentially of that instrument plus a camera and usually an independent light source.

There are two main types of apparatus, the simpler one being an attachable cone camera complete with double dark slide and focusing screen, or the more elaborate optical bench in which the axis of light transmission, microscope and camera lens is disposed horizontally.

In the simpler pattern, the cone is usually of aluminium and is 7 in. long. At its wider end it is attached to a mahogany frame carrying the focusing screen and double dark slide for $3\frac{1}{4}$ in. \times $3\frac{1}{4}$ in. plates (lantern size). Other sizes are available. The microscope is set up in a vertical position and the lower end of the cone fits over

¹ A. H. Bennett, H. Jupnik, H. Osterberg, O. W. Richards, *Phase-Microscopy: Principles and Applications*, (John Wiley, New York), 1951, p. 225.

See also *Photography through the Microscope*, (Eastman Kodak Co., Rochester 4, New York and London), 1952, p. 55.

the upper part of the body-tube where it is tightly clamped. The operation of this type of apparatus is relatively easy in the hands of amateur photographers and some exceedingly good results can be obtained with minimum time and expense.

In the optical bench version, which incidentally takes up much more space than the cone attachment, the microscope is placed horizontally and provision is made for the independent units, camera, microscope, lenses, filters and light-source to be separately mounted by clamps on a square cross-section bar, so that they can be moved into desired positions. With this kind of bench in use in the author's laboratories, adjustments of alignment and position are possible to exceedingly fine limits. This apparatus is, however, time-consuming in preparation and essentially professional in operation. A further use for this bench is for projecting slides of minerals, rocks, etc., directly on to a matt white screen for demonstration and other purposes. For further information, the reader is directed to the references below¹.

SYSTEMATIC EXAMINATION OF SEDIMENTARY ROCK MINERALS UNDER THE MICROSCOPE

A systematic investigation of sedimentary rock minerals is strongly recommended, until by experience the student has become proficient in the art of recognizing and discriminating between associated species. The plan of procedure may be summarized as follows:

1. *With transmitted white light, low and high-power objectives.*
 - (a) Transparency, translucency or opacity.
 - (b) Colour.
 - (c) Habit. Presence or absence of crystal faces.
 - (d) Shape. Angular, subangular, rounded.
 - (e) Size. Estimate or measure with eyepiece micrometer.
 - (f) Fracture. Uneven, conchoidal, etc.
 - (g) Parting. Linear or irregular.
 - (h) Cleavage. Principal and subordinate directions.
 - (i) Abrasion, degree of. Pitting or other surface features.
 - (j) Refractive Index. Compare with Canada Balsam (1.54).

¹ J. E. Barnhard and F. V. Welch, *Practical Photomicrography*, 3rd. ed. (Longmans, Green, London), 1936.

W. H. S. Cheavin, *Photomicrography: Methods and Apparatus*, The Modern Encyclopedia of Photography, (Amalgamated Press, London), vol. 11, p. 1000.

H. L. Hind and W. B. Randles, *Handbook of Photomicrography*, 2nd ed. (E. P. Dutton and Co., New York), 1927.

A. Jackson, *Amateur Photomicrography with Simple Apparatus*, 4th ed. (The Focal Press, London), 1945.

Photography through the Microscope, (Eastman Kodak Company, Rochester 4, New York and London), 1952.

- (k) Thickness of grains.
 - (l) Inclusions.
2. *With reflected light against dark background to slide (dark ground illumination).*
 - (a) Lustre. Adamantine, metallic, submetallic, vitreous, resinous, etc.
 3. *With transmitted light, polarizer only inserted.*
 - (a) Pleochroism. Presence or absence. Weak or strong. Colour change with orientation of grain. 'Twinkling' as indicative of carbonates (rotation of polarizer only).
 4. *With transmitted light, crossed nicols.*
 - (a) Isotropism or anisotropism.
 - (b) Birefringence.
 - (c) Extinction. Straight or oblique; in latter case determine angle.
 - (d) Interference colours: order, etc. (with quartz wedge or other device).
 - (e) Relative retardation and vibration directions (with quartz wedge, gypsum plate, etc.).
 5. *With convergent light, high power objectives, crossed nicols and Bertrand lens.*
 - (a) Detection of interference figure: uniaxial or biaxial.
 - (b) Determination of the sign of the crystal by means of a quartz wedge, gypsum or mica plate.
 - (c) Optic axial angle.
 - (d) Dispersion of optic axes.

NOTES

1. (a)–(i). Most of these physical determinations are straightforward. Translucent minerals can frequently be rendered more transparent by inserting the condenser; similarly opaque minerals may be rendered slightly translucent on thin edges, *e.g.* sphalerite, chromite. Cleavage may be an important diagnostic property, especially in thin sections, *e.g.* amphiboles and pyroxenes, where two sets of cleavage lines may intersect at given angles. Many detrital minerals tend to exhibit conspicuous cleavage, *e.g.* kyanite, topaz, calcite, fluorite. Degree of abrasion and shape of grains are important factors in the study of heavy mineral residues for correlation (see Vol. II, Ch. V).

1. (j). *Refractive Index.*—The most common method of determining relative refractive index is that known as the method of central illumination or Becke's 'White Line' method, generally applicable, but particularly to minerals in thin section and to platy detrital grains (Fig. 26). The test is as follows: If the mineral under observation has a *higher* R.I. than a contiguous mineral or mountant such as Canada Balsam (R.I. 1.54) then on *raising* the objective a 'white line' (*i.e.* apparent periphery or boundary of the mineral) will contract inwards, *i.e.* away from the contact substance or medium of lower R.I. (N.B. A good

mnemonic is to connect in the mind the words '*high*' and '*raise*'.). Conversely, if the mineral under observation has a lower R.I. than a contiguous mineral or mountant, then on raising the objective the 'white line' will expand outwards, *i.e.* into the substance or mountant of higher R.I. Fig. 26 makes these conditions clear. If the mineral and contiguous substance or mountant have identical refractive indices, the contact is practically invisible and the 'white line' effect is reduced to a minimum.

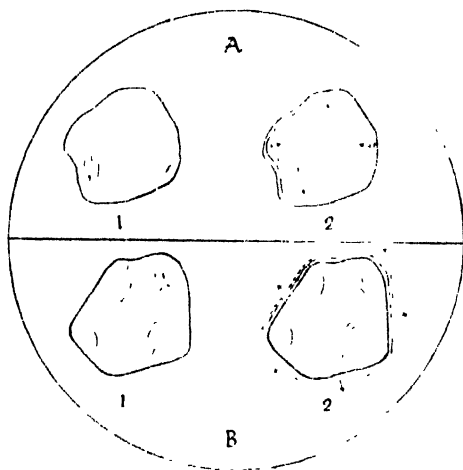


FIG. 26. Diagram to illustrate Becke's Line R.I. Test.
Medium: Canada balsam.

- A. 1. Topaz grain in correct focus.
- 2. Same with objective raised: margin travels inwards.
- B. 1. Fluorite grain in correct focus.
- 2. Same with objective raised: margin travels outwards.

Lowering instead of raising the objective reverses the above effects. Use the concave mirror when making the test. In some cases manipulation of the iris diaphragm is advantageous. Do not, however, use the condenser. Another method is that of oblique illumination, or Schroeder van der Kolk's method. This requires some degree of skill to effect successfully and is carried out with isolated grains or mineral fragments either mounted in Canada balsam or immersed in a solution of known R.I. For a description of this method see p. 246.

1. (*k*). Thickness of Grains.—This measurement is generally carried out on unmounted material. Make a mark on a glass slip with a diamond and focus the mark with the microscope. Place the grain over the mark and focus its upper surface (turn micrometer screw in same direction throughout). The difference in readings gives the thickness required. Another method is to focus the surface of the grain placed over a mark,

then focus the mark through the grain; in this case if the refractive index of the mineral is known, $T = nt$, where T = actual thickness, n = refractive index and t = measurement of difference in the two readings of the micrometer screw.

In the case of mineral grains forming part of a residue mounted in Canada Balsam on a glass slip, approximate thickness of a grain can usually be estimated by focusing its lower surface (boundary-edge if coloured or translucent) and then its upper surface (centre of grain); the difference between the two readings as recorded by the micrometer screw gives the desired information, allowance being made for the R.I. as before.

Thickness of Rock Sections.—A satisfactory thickness for thin sections is 30μ . Thickness of a mineral slice in microns is equal to the interference colour value (p. 236) divided by 1,000 times birefringence (p. 234). Hence it is necessary to choose a common mineral in the slice, the birefringence of which is known, *e.g.* quartz, $B = 0.009$. Examine a number of quartz components in the slice and estimate the highest interference colour (in $\mu\mu$) revealed by comparison with a standard interference or polarization colour chart, *e.g.* that by W. R. Jones and A. Brammall¹.

Example. Search of a series of quartz components shows 1st order yellow as highest interference colour value (say) $400\mu\mu$. Hence thickness of slice T (in μ) is given by:

$$T = \frac{400}{1000 \times 0.009}$$

$$= 44\mu \text{ or } 0.044 \text{ mm.}$$

Where slices are of uniform thickness, determined as above, associated minerals may be diagnosed with reference to their birefringence values (Vol. II). This is particularly useful when dealing with well-made rock-slices, where the quartz components are all exhibiting 1st-order grey interference colours. The problem is not quite so easy, however, when the slice is of varying thickness (attested by quartz particles of high 1st-order or even 2nd-order colours), especially in central portions of rocks which have presented difficulty in slicing.

1. (I). Inclusions.—The study of inclusions in mineral grains is important from a crystallographic standpoint and also it is frequently of diagnostic value. Inclusions should be classified not only as regards nature, but also according to frequency, orientation, size, etc. Inclusions may be solid, *i.e.* definite mineral species; rarely liquid; or may be gaseous or air-filled chambers; or often glass. Search, if necessary, with the highest power magnification available.

2. (a). For observations with dark ground illumination, refer to paragraphs (a), (b) and (c) on p. 213 also to p. 220.

3. (a). Direction of maximum absorption should be carefully determined, also whether fast or slow: see below, para. 4(e). Pleochroism is

¹ Published by J. Swift & Co., London.

best seen by rotating the nicol rather than the stage. The use of the high-power objective and convergent light is extremely helpful where the phenomenon is only weakly displayed. Note the diagnostic value of 'twinkling' in connexion with rhombohedral carbonates (observed by rotating the polarizer only). Pleochroic haloes are best investigated with high-power objective and the convergent system (Pl. 8).

4. (a). Isotropism.—The real test of isotropism is to try for an interference figure. Remember that basal sections of certain minerals will appear isotropic between crossed nicols, but may still give interference figures, hence such minerals are *not* isometric, e.g. anatase, tourmaline, quartz. Isometric minerals in the absence of strain phenomena are definitely isotropic and cannot possibly yield interference figures.

4. (b). Birefringence.—This is particularly important in rock minerals, whether in thin sections or as isolated grains and should be determined correctly wherever diagnosis is doubtful, if such determination is at all possible.

Birefringence may be defined as the amount of retardation in velocity between the slow and fast light vibrations per unit distance through a crystal. Such retardation is expressed in micromillimeters ($\mu\mu$). It is numerically represented also by the difference between the two refractive indices of a uniaxial mineral (*infra*), either ϵ (extraordinary ray) being less than ω (ordinary ray) or *vice versa*; with biaxial minerals it is always the difference between the maximum and minimum values of refractive index, i.e. $\gamma - \alpha$ ($\alpha < \beta < \gamma$).

Example 1. Uniaxial Mineral. Quartz.

R.I. $\epsilon = 1.553$, $\omega = 1.544$.

Birefringence $\epsilon - \omega = 0.009$, or $9\mu\mu$ per micron thickness of slice.

Suitable thickness for thin sections = 30μ .

\therefore Total relative retardation due to quartz section 30μ thick = $30 \times 9 = 270\mu\mu$; this is equivalent to 1st-order yellowish white interference colour.

Example 2. Biaxial Mineral. Kyanite.

R.I. $\alpha = 1.712$.

$\beta = 1.720$.

$\gamma = 1.728$.

Birefringence $\gamma - \alpha = 0.016$ or $16\mu\mu$ per micron thickness of slice.

Suitable thickness for thin sections = 30μ .

\therefore Total relative retardation due to kyanite section 30μ thick = $30 \times 16 = 480\mu\mu$. This is equivalent to 1st-order red interference colour.

The relationship between birefringence, thickness of mineral and interference (polarization) colour value is given by:

$$B = \frac{I}{T \times 1000}$$

where B = birefringence measured in $\mu\mu$, I = interference colour value (in $\mu\mu$), T = thickness ordinarily measured in microns (μ) or $\times 1,000$ in micromillimeters ($\mu\mu$). Thus it is clear that, knowing any two of these functions, the third may be calculated.

The diagnostic value of birefringence will be obvious from the above considerations, since if this value for a mineral in thin section or of a detrital grain can be fixed definitely, or even if within reasonable limits, reference to a table such as given in Vol. II, Appendix VII, will enable the species to be run down with a fair degree of certainty.

Procedure for thin sections is to determine thickness and interference colour value as described on p. 233 and with reference to a polarization colour scale, using the formula given above. For isolated grains, procedure is necessarily different.

As is well known in work on detrital quartz, for instance, those grains which do not show emergence of the optic axis and are therefore not isotropic, exhibit interference colours generally in the form of concentric coloured bands or rings. These bands correspond to zones of different thickness of the grain, usually increasing from the periphery to the centre. By selecting a prominent colour such as red and noting the number of red rings from the edge to the centre of the grain, reds of the first and second orders may be distinguished or, if sufficiently thick, corresponding 3rd- and 4th-order pinks may be revealed; the order being thus known may be fixed approximately in terms of its birefringence ($\mu\mu$) and thus thickness calculated as above. It must be admitted that often detrital grains are too variable in thickness or possibly too thick at the centres to reveal lower order colours; alternatively, the natural colour of the mineral may mask the interference tint; in such cases it is not possible to employ this procedure and other methods of diagnosis become necessary.

4. (c). Extinction.—Rock minerals other than those crystallizing in the isometric system and (exceptionally) sections or grains showing emergence of an optic axis, are anisotropic and normally exhibit interference colours between crossed nicols.

Such minerals, apart from occasional abnormalities of monoclinic and triclinic crystals, exhibit extinction ('black-out') at regular intervals of 90° during one complete rotation through 360° . Extinction positions imply coincidence of directions of light vibration in the mineral with those of the analyser and polarizer.

Parallel extinction (straight extinction) is when these directions are parallel to crystal face-boundaries, crystallographic axes, cleavage or twin planes. Symmetrical extinction implies a position bisecting the angle between two crystal faces, cleavage planes, etc. Both forms are exhibited by all tetragonal, rhombohedral and orthorhombic minerals and by those monoclinic mineral sections or grains which parallel the b -axis (Pl. 8).

Oblique or inclined extinction is characteristic of monoclinic (exception above) and all triclinic minerals (in rare cases no real extinction as such may be discerned) and the angle measured between such an extinction position and a prominent crystal boundary, cleavage or twin plane is

the extinction angle for that particular mineral section or grain. Measurement of the extinction angle is of considerable diagnostic value, *e.g.* plagioclase feldspars, kyanite, hornblende (Pl. 8).

4. (d). *Interference Colours.*—The colours of anisotropic minerals (thin sections or grains), when examined in polarized light, result from interaction of fast and slow light vibrations through such minerals, the phenomenon being known as 'interference'. Such colours are a function of (a) differential velocities of the fast and slow rays and (b) thickness of the section or grain involved. To appreciate the succession of interference colours ranging from 1st to 4th and perhaps higher orders, the best plan is to study a quartz wedge between crossed nicols. This will (if properly made) reveal the colour bands transverse to the length of the wedge, as shown in Fig. 25.

Methods of determining the order of interference colour:

- (i) *By inspection.* Familiarity with rock minerals and optical measurements thereon, both in thin sections and as grains, enables a reasonably accurate assessment of the colour or shades of colour sequence to be made and thus its position in the lower orders fixed. Remember that the natural colour of a mineral, especially in detrital grains and if dark, may make such visual assessment difficult, even erroneous; in such cases more precise measurements should be undertaken if possible.
- (ii) *By matching with a polarization colour scale.* Such scales are reproduced in various textbooks, but most usefully in the pocket scale by W. R. Jones and A. Brammall¹, which not only shows the sequence of the first four order colours as revealed by crossed nicols but also the corresponding colours revealed with parallel nicols, the latter forming a definite check on identification of the former.
- (iii) *By determining relative retardation, i.e. interference colour value,* if thickness and birefringence are known ($I = 1,000BT$, where I = interference colour value in $\mu\mu$, B = birefringence (in μ), T = thickness (in μ).
- (iv) *By means of a calibrated quartz wedge* (p. 225). The mineral is orientated in such a position that when the quartz wedge is superimposed by means of the slot in the body-tube of the microscope (between the analyser and polarizer), the interference colour of the mineral is lowered in its order until *compensation* occurs, *i.e.* grey or black (isotropism), corresponding to positions in the wedge and mineral where the relative retardations are the same for both, or have the same numerical value zero. The succession of colours traversed till the black band appears is a measure of the order of the original interference colour of the mineral and with the wedge suitably calibrated this can be closely assessed in most cases. A gypsum or mica plate (p. 224) of known orientation can be used in the same way.

¹ See p. 233.

4. (e). **Relative Retardation and Vibration Directions.**—As will be evident from the foregoing notes on birefringence (p. 234) and interference colours (p. 236), relative retardation is the amount of 'lag' of the slow ray behind the fast ray in a crystal and may be conveniently expressed as the product of birefringence and thickness, *i.e.* $R = 1,000BT$, where R is always expressed in $\mu\mu$, B and T usually in μ . Relative retardation in $\mu\mu$ values corresponds to specific interference colours as revealed under crossed nicols, such values being grouped into 1st, 2nd, 3rd, 4th orders and so on (Fig. 25), and being multiples of $550\mu\mu$.

Determination of relative retardation is made:

- (i) Approximately by inspection of the interference colour. This is a matter of practice and recognition of the order of the particular interference colour observed. Reference to a polarization colour scale is desirable¹, also check of the colour exhibited with parallel nicols as against normal tint with crossed nicols.
- (ii) More precisely with a quartz wedge. Orientate the mineral at 45° to its extinction position. Using a wedge with length slow (ϵ), insert in the slot in the body-tube between the polarizer and analyzer. The interference colour due to the mineral is either raised or lowered in its order. If raised, the slow directions of the wedge and of the mineral coincide, *i.e.* the slow direction of the wedge is parallel to that of the mineral; the retardation in this case 'plus'. If lowered, then the slow direction of the wedge and of the mineral are opposed, *i.e.* the slow direction of the wedge is parallel to the fast direction of the mineral; the retardation in this case is determined by using a calibrated quartz wedge and noting the succession of colours traversed till the zero position (black band) is observed, *i.e.* compensation.

A gypsum plate is employed with advantage in cases where there is low relative retardation. Knowing the character of the length of the compensator (usually fast), that of the mineral under examination may be determined by noting whether the colours are raised (fast) or lowered (slow) when the plate is superimposed on the mineral. A mica plate may be similarly used.

5. (a). **Interference Figure (Directions Image).**—To obtain an interference figure with the ordinary petrological microscope, use the high power objective, convergent system, crossed nicols and Bertrand lens, with really good illumination; the iris diaphragm in the substage system carefully manipulated may aid definition. A much clearer figure with detrital grains is often procurable by removing the eyepiece and dispensing with the Bertrand lens. Sometimes the figure is better appreciated by holding the eye a little distance away from the body-tube aperture (eyepiece removed). It is a good rule to practice with specially cut mineral-sections which give complete figures, carrying out the necessary observations with quartz wedge, gypsum or mica plate on known substances; this familiarizes the observer with the phenomena under the best conditions

¹ See p. 233.

and serves to prepare his eye for less clearly defined figures, such as are often characteristic of detrital grains. *This optical property should be thoroughly mastered at the outset: it is an invaluable test in the diagnosis of detrital and many rock-forming minerals.*

The interference figure may be uniaxial (Fig. 27) or biaxial (Fig. 28). Complete *normal* uniaxial figures are yielded by minerals crystallizing in the tetragonal, rhombohedral and hexagonal systems, presenting sections or grains at right angles to the optic axis. Such figures consist of

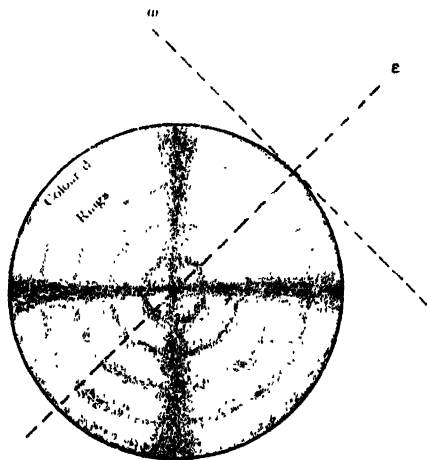


FIG. 27. Uniaxial Interference Figure.

concentric coloured rings (isochromatic lines) surmounted by a black cross formed by the isogyres which does not break up on complete rotation of the stage through 360° . In very thin sections or grains, the coloured rings may be replaced by a grey-blue background. Biaxial figures are yielded by minerals crystallizing in the orthorhombic, monoclinic and triclinic systems, presenting sections or grains at right angles to the acute bisectrix, *i.e.* the bisector of the acute angle between the two optic axes of such minerals. Such figures assume different complexions according to orientation; in the 90° position (Fig. 28A) the two isogyres unite to form a kind of black cross surmounting coloured lemniscates, similarly for the 0° , 180° and 270° positions. In the 45° , 135° , 225° and 315° positions, the cross splits up into two curved isogyres opposing each other and convex inwards, surmounting coloured lemniscates as before. Fig. 28C shows this. Both pseudo-biaxial and pseudo-uniaxial figures are sometimes displayed, in the former case a known uniaxial mineral exhibiting a black cross which just 'parts' at the centre on rotation, *e.g.* some varieties of quartz, and in the latter case a known biaxial mineral of exceedingly small optic axial angle only just shows the slight parting of the

isogyres in the 45° position, *e.g.* some varieties of biotite. A 'compass-needle' figure, *i.e.* one isogyre rotating about a central point as the stage is turned, is yielded by the emergence in a crystal section of one optic axis (biaxial mineral), *e.g.* the basal plane of epidote. Partial figures, common with many detrital flakes, constitute special cases for both uniaxial and biaxial minerals and are sometimes not easy of interpretation.

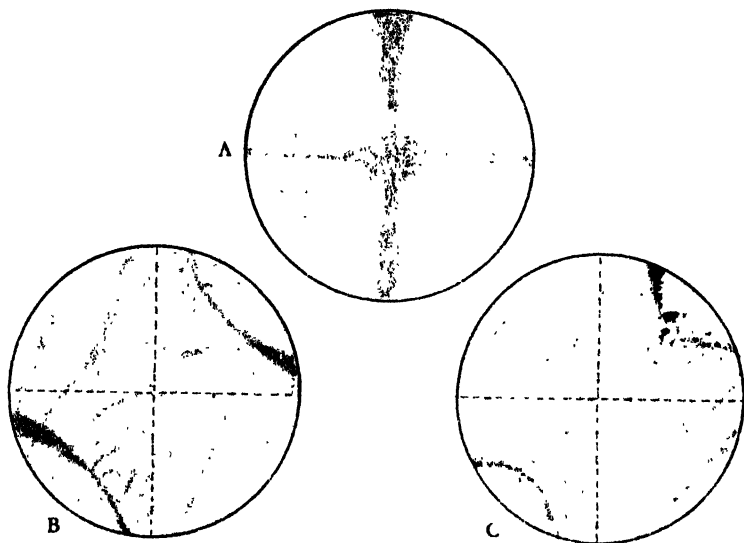
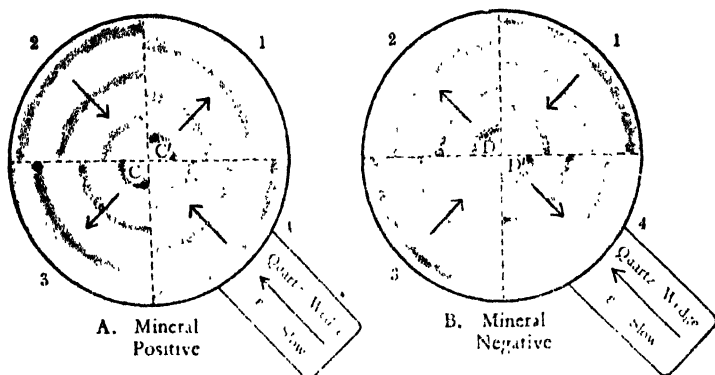


FIG. 28. Biaxial Interference Figures. A. 90° Position; B. $22\frac{1}{2}^\circ$ Position; C. 45° Position.

5. (b). Determination of the Sign of a Mineral. Uniaxial Mineral.—This has two indices of refraction, ϵ and ω , corresponding to the extraordinary and ordinary rays respectively. ϵ Vibrations are in the plane containing the optic axis, ω vibrations in a position at right angles to this. If $\epsilon > \omega$, ϵ is slow and the mineral is positive; if $\omega > \epsilon$, ϵ is fast and the mineral is negative. Use a quartz wedge (long direction ϵ slow)¹ and insert it in the slot of the body-tube of the microscope at 45° to the black cross. The effect of the quartz wedge is to cause the cross to break up, apparently into two prominent black 'spots', aligned in a definite direction, either parallel or normal to direction of insertion of the wedge; at the same time the coloured rings are distorted, expanding in one direction (with the 'spots') and contracting in the other at right angles thereto. If the cross breaks into two apparent black 'spots' in quadrants 1 and 3 (Fig. 29A) with corresponding expansion of the rings in those quadrants, it will

¹ N.B. Use gypsum plate in cases of low relative retardation, where coloured rings are not apparent or a blue-grey 'background' to cross persists. Quartz wedges are also cut with length fast ω ; in this case observations will be reversed (see p. 225).

be found that the rings contract towards the centre in quadrants 2 and 4, *i.e.* along the line of insertion of the wedge; the mineral is then positive. When the opposite movements take place, *i.e.* expansion outwards in quadrants 2 and 4 (along the line of insertion of the wedge) and contraction inwards in quadrants 1 and 3, the mineral is negative (Fig. 29B). A good mnemonic for remembering this is that with a positive mineral an imaginary line joining the two black spots makes a *plus* sign with the length of the quartz wedge as inserted; if negative, the line coincides with the length of the wedge and a *minus* sign is suggested.



The arrows within the field show the directions in which the coloured rings move as the wedge is pushed into the slot.

Two black spots (indicating compensation) appear at C and C', and develop into quarter circles moving outwards.

The arrows within the field show the directions in which the coloured rings move as the wedge is pushed into the slot.

Two black spots (indicating compensation) appear at D and D', and develop into quarter circles moving outwards.

FIG. 29. Effects of Superimposing Quartz Wedge on Uniaxial Figures.¹

The foregoing method of determining sign, though empirical, is none the less reasonably accurate, especially where the directions image is complete and clear and in cases where the colours are not easily discernable, which is by no means unusual with detrital grains. Where the image is indistinct or partial and whenever the colours can be interpreted correctly, the more accurate procedure is to note the effect of inserting the quartz wedge (or other compensator) on the colours in the visible quadrants, as when determining order of interference colour (p. 236) or relative retardation (p. 237). Figs. 29A and B illustrate the two possibilities.

When the mineral is *positive* ϵ is slow; the length of the wedge being slow (ϵ), the coloured rings contract inwards in the direction of insertion

¹ The drawings of Figs. 29 and 32 were prepared from observations made with a slow 'mica step'. For all practical purposes the appearances are identical, although the quartz wedge (particularly if it is a steep one) produces a certain amount of distortion of the figure.

of the wedge and expand in a direction at right angles to this. Simultaneously the colours are raised in their order in the two quadrants 2 and 4 in the path of the wedge (where slow direction of the mineral coincides with slow direction of the wedge) and are lowered in the other two quadrants 1 and 3.

When the mineral is *negative* ϵ is fast; the length of the wedge being slow (ϵ), the coloured rings expand outwards in the direction of insertion of the wedge and contract inwards in a direction at right angles to this. Simultaneously the colours are lowered in their order in the two quadrants 2 and 4 in the path of the wedge (where the fast direction of the mineral coincides with slow direction of the wedge) and are raised in quadrants 1 and 3.

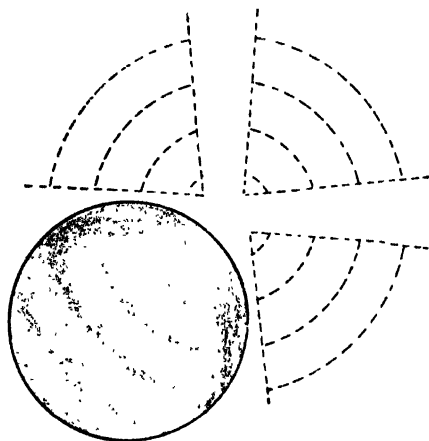


FIG. 30. Partially developed Uniaxial Interference Figure.

In the case of partially developed uniaxial interference figures, *i.e.* where section or grain-face is inclined to the optic axis at any angle up to 90° (when it is parallel thereto), interpretation of the directions image has in most cases to be made on the basis of colour reaction to the compensator, although sometimes a uniaxial mineral will exhibit on complete rotation first a horizontal black band (isogyre), then a vertical band, then a horizontal and finally a vertical band, moving successively into position, rigidly and without curvilinear or sweeping movement across the field; the optic axis in such cases usually lies outside the field of view, but the uniaxial character of the mineral is none the less suggested (Fig. 30).

Where the inclination does not reach a maximum and a 'quadrant' is discernible, the locus of the optic axis outside the field is not difficult to visualise; the quartz wedge superimposed on this quadrant then has the effect of raising or lowering the colours; in the former case the mineral is positive, in the latter case it is negative. In the extreme case where the

section or grain-face is parallel or nearly so to the optic axis, the locus of the optic axis can usually be estimated by appeal to the coloured bands displayed, the highest order colours being nearest to the locus, the lower order colours following successively away from it in the direction of the extraordinary ray ϵ . Determination of slow or fast direction is made in the usual way with a quartz wedge and the sign of the mineral thus obtained.

Biaxial Mineral.—Biaxial minerals have three indices of refraction, α , β and γ ($\alpha < \beta < \gamma$) and, as the adjective implies, two optic axes, which are related as shown in Fig. 31. If the bxa coincides with γ (Z), the mineral is said to be *positive*; if it coincides with α (X), the mineral is *negative* (Z = slow, X = fast vibration directions).

The sign may be determined in one of the following ways:

- (a) The mineral is *positive*: the isogyres *appear* to move towards each other along the line of insertion of the wedge and the colour-bands move in the directions indicated in Fig. 32A. The mineral is *negative*: the isogyres *appear* to retreat outwards along the line of insertion of the wedge, i.e. 'repel' each other, the colour-bands moving as in Fig. 32B. This method is, however, somewhat empirical.
- (b) Orientate the figure in the 45° position. The mineral is *positive*: the effect of inserting the quartz wedge (length slow) is to raise the order of the colours due to the mineral within the concave space enclosed by each isogyre and to lower the order of the colours in the intervening space between the convex sides of the isogyres. The mineral is *negative*: the effect of inserting the quartz wedge as above is just the reverse; lower colours are produced within the concave space enclosed by each isogyre and higher colours in the intervening space between the convex sides of the isogyres. This method is not always conclusive where the isogyres are placed far apart near the boundaries of the field of view or where the colour of the mineral is deep.
- (c) Orientate the figures in the 45° position; the axis of the isogyres is the trace of the obtuse bisectrix (bxo) and its fast or slow vibration character is determined with the quartz wedge in the usual way. The mineral is *positive*: the bxo is fast and corresponds to α or X; the acute bisectrix (bxa) is at right angles to this axis and therefore corresponds to γ or Z. The mineral is *negative*: the bxo is slow and corresponds to γ or Z; the bxa is therefore fast and corresponds to α or X.

Where a mineral section or grain-face is inclined to the acute bisectrix, one isogyre (or part thereof) may be observed which moves across the field as the stage is rotated, becoming most prominent when the 45° position is reached. The convex side of the isogyre then faces the bxa and thus the axis of the isogyres is fixed. The fast or slow character of this axis is then measured as described above and thus the sign of the mineral deduced.

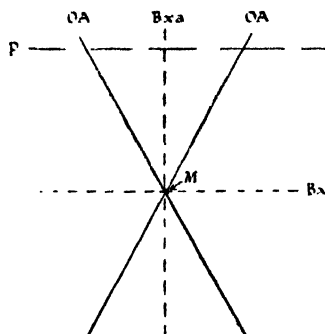
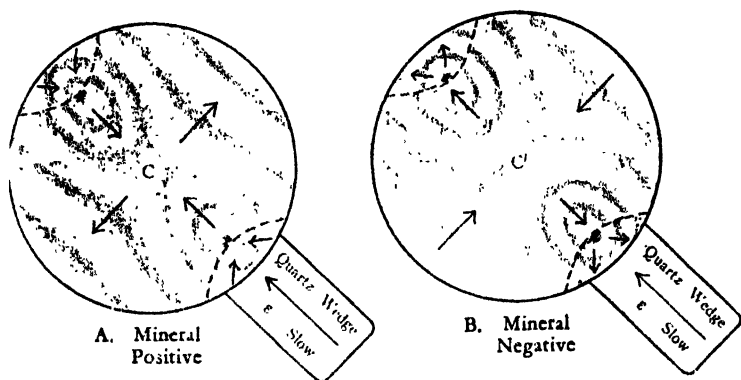


FIG. 31. Diagram of Optic Axial Plane, etc.

OA, Optic axis; Bxa, Acute bisectrix; Bxo, Obtuse bisectrix; PP, relative orientation of crystal section which will exhibit a biaxial interference figure; M, Third Mean Line (Optic Normal) at right angles to plane of paper.



The arrows within the field show the directions in which the colour-bands move as the wedge is pushed into the slot.

At C the colours change in *descending* order of Newton's scale until compensation (black) is obtained, after which they change in *ascending* order.

The arrows within the field show the directions in which the colour-bands move as the wedge is pushed into the slot.

At C' the colours change in *ascending* order of Newton's scale.

FIG. 32. Effects of Superimposing Quartz Wedge on Biaxial Interference Figures.

Certain minerals, *e.g.* epidote, exhibit what are sometimes termed 'compass-needle' figures as previously mentioned (p. 239), consisting of one isogyre rotating about a central 'point' as the stage is turned; this 'point' is, in fact, the emergence of one of the optic axes; such figures constitute special cases where the optic axial angle approaches 90° . In other cases, depending on magnitude of the optic axial angle, a mineral section or grain-face normal to one optic axis may show a straight or curved isogyre according as it is orientated in the 0° or 45° positions. Such characteristics may in themselves be of significance in confirming identity of the mineral.

Finally, any biaxial mineral section or grain-face parallel to the *bxa* or optic axial plane may reveal a figure not unlike that of a uniaxial mineral parallel to its optic axis. In such a case determination of sign depends largely on clarity of the colours and separation of lower from higher-order groups if properly developed in opposite parts of the field of view. Where the lower-order colours can be correlated with a definite direction, this direction is the *hxa* and a quartz wedge is all that is necessary to determine whether the direction is slow (positive) or fast (negative).

Generally, if some kind of interference figure is revealed, however indifferent in outline or colour value, some useful evidence can be deduced from it, especially by making good use of the quartz wedge and other compensators. Admittedly, detrital minerals often present great difficulties in this respect, not only in cases where the particular grain shows nothing at all (or at least nothing decipherable), but where natural colour, inclusions, superficial staining or alteration products may mask any inherent optical effects. For all practical purposes the information given in this book should suffice, but in special cases where the student is minded to probe this branch of optical physics more deeply, he would be well advised to consult the references below¹.

5. (c). Optic Axial Angle.—There are various methods of measuring or calculating axial angles where suitably cleaved detrital minerals, crystal fragments of specially prepared sections normal to the acute bisectrix exhibit reasonable biaxial interference figures. A common procedure is to measure or estimate the distance separating the convex sides of opposing isogyres when the crystal is orientated in the 45° position, applicable when the axial angle is not too large. For this purpose a micrometer with co-ordinate ruling and fitted into the ocular of the microscope is usually employed. Alternatively, a microscope fitted with a universal stage is employed for more precise measurements of this character (p. 226).

¹ J. W. Evans, *The Determination of Minerals under the Microscope*, (Murby, London), 1928.

A. F. Hallimond, *Manual of the Polarizing Microscope*, (Cooke, Troughton and Sims, York, England), 1953.

E. E. Wahlstrom, *Optical Crystallography*, 2nd ed. (Wiley, New York), 1951.

A. N. Winchell and H. Winchell, *Elements of Optical Mineralogy*, (Wiley, New York), 1951.

If the values of the three refractive indices α , β and γ are known, then the optic axial angle can be calculated by the following formula:

$$\tan^2 V\gamma = \frac{\frac{1}{\alpha^2} - \frac{1}{\beta^2}}{\frac{1}{\beta^2} - \frac{1}{\gamma^2}}.$$

In cases where a mineral presents a face or surface normal to one optic axis, it is possible to estimate the optic axial angle by scrutiny of the amount of curvature of the isogyre. If the latter appears horizontal in the 45° position, the axial angle approximates 90° ; it decreases according as the degree of curvature is observed to increase.

For fuller particulars of such measurements, reference should be made to the works cited on p. 244.

5. (d). Dispersion of Optic Axes.—The optic axial angle may be greater or less according as red or violet light is used and this is indicated conventionally by

$$\rho > \text{or} < \nu$$

There are two general cases:

- (a) Orthorhombic minerals and those monoclinic minerals in which the optic axial plane includes the b-axis: the hyperbolæ (of the interference figure) show the same amount of dispersion.
- (b) Other biaxial minerals: dispersion may be different for each optic axis.

In the case of (a) assuming $\rho < \nu$ and representing moderate dispersion, a red colour is noted on the concave side of the isogyre and a blue on the convex side; conversely when $\rho > \nu$ with strong dispersion the black isogyres give place to a series of coloured bands.

In the case of (b), dispersion of each optic axis should be determined separately or alternatively the optic axial angle should be measured using different coloured light¹.

DIAGNOSIS OF MINERALS BY REFRACTIVE INDEX (IMMERSION) METHOD

Attention is now directed to this method of precise refractive index determination as a basis of identification of mineral grains and fragments². The method is invaluable for confirmatory diagnosis of individual mineral particles, but it is obviously unsuited as a means of determining and comparing composite assemblages of heavy minerals for stratigraphical purposes, though this has actually been suggested in some quarters. As W. A. Tarr once

¹ E. S. Larsen and H. Berman, *U. S. Geol. Surv., Bull.* 848, 1934, p. 22.

² E. S. Larsen, *The Microscopic Determination of Non-Opaque Minerals*, *U.S. Geol. Surv., Bull.* 679, 1921; also with H. Berman, *U.S. Geol. Surv., Bull.* 848, 1934.

said¹, 'the predominating factor in the study of sediments in Europe is the use of the microscope'; the tendency everywhere today is undoubtedly to rely primarily on microscopical analysis, reserving special optical, micro-chemical or spectroscopic tests for doubtful individual cases. On the other hand, immersion methods can be employed with advantage not only as a basis of accurate optical measurements but, in cases of doubtful diagnosis, to narrow down possibilities accurately and speedily.

The determinations are most conveniently made by immersing a given mineral fragment or detrital grain in a drop of the selected refractive index liquid on a glass slip and observing their relative relief under the microscope; application of the Becke test (p. 232) will indicate whether the mineral possesses a higher or lower refractive index than that of the fluid in which it is immersed. When the refractive indices of the mineral and of the medium are in accord, the former is practically invisible. A glass slip with bowl-shaped hollow, similar to that recommended for mounting coarse material (p. 107) is a convenient form of mount for this purpose.

The most satisfactory and commonly applied procedure in determining refractive index of a mineral grain, employing a liquid or other medium of known R.I. as mountant, is that known as the method of oblique illumination, or Schroeder van der Kolk's method. Comparison is made by observation of the contact between the grain and the medium while part of the field is shaded; this is best achieved by inserting the finger or a piece of card below the stage of the microscope².

(i) Using a low-power objective and no condenser the results are as follows:

- (a) Where the grain has a much higher R.I. than the medium, it will present a shadow or dark border towards the side at which the card is introduced and a bright border on the opposite side (Fig. 33A).
- (b) Where the grain has a much lower R.I. than the medium, it will present a shadow or dark border on the opposite side to that at which the card is introduced and a bright border on the other side (Fig. 33B).
- (c) Where the grain has a R.I. approximating that of the medium, the border is observed to be coloured, blue on one

¹ W. A. Tarr, *Studies of Sediments in European Laboratories*, National Research Council, *Researches in Sedimentation* in 1924, 1925, p. 35.

² F. Smithson, in a written communication, suggests that, where a slot is provided just above the objective, a glass plate, blackened except for an aperture of about 8 mm. diameter, may be used to produce darkness over half the field. Using this method, a grain of high R.I. gives a dark border towards the dark side of the field.

side, red on the other. With monochromatic light and transparency, the grain will practically, if not entirely, disappear. The stronger the dispersion of the medium employed, the greater the tendency for the red and blue borders to develop, even when the R.I. of both grain and medium differ only slightly for monochromatic light.

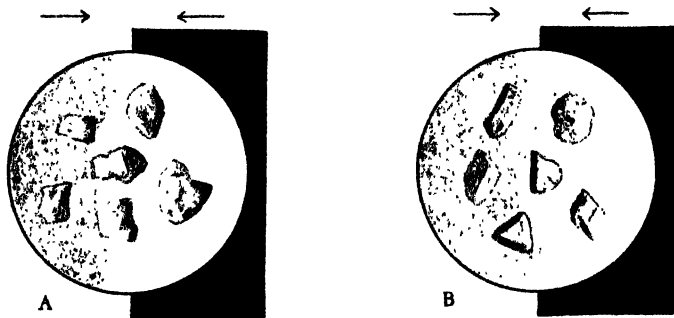
(ii) If a high-power objective and the condenser are used, the reaction will depend on the position to which the latter is screwed up. Assuming the focus of the condenser lens to be *above* the grain, then the effects noted in (a), (b) or (c) as described will operate. If the focus of the condenser lens is *below* the grain, the effects are reversed.

Shadow in the field comes in from the left.

Card introduced from the right below the stage.

Shadow in the field comes in from the left.

Card introduced from the right below the stage.



R.I. of the grains is higher than that of the medium. Grains are dark on the same side as that on which the card is introduced.

R.I. of the grains is lower than that of the medium. Grains are dark on the side opposite to that from which the card is introduced.

FIG. 33. Immersion Method of R.I. Determination. A. Almandite. B. Fluorite. Both in Clove Oil. R.I. 1.53.

As this method is applicable not only to detrital grains but also to rock minerals in thin section, it should be mastered at the outset of petrographic studies, even though it may take time and practice to accustom the eye to the phenomena. It is a good plan to experiment first with a low-power objective, no condenser, mineral grains of known R.I. and a medium (say Canada balsam, cinnamon oil or bromoform) to illustrate each of the conditions (a), (b) and (c) above. Thereafter the process should be repeated, using the high-power objective and the condenser system to check both possibilities of focal position of the latter. Furthermore, it is advisable to keep at hand mounts, *e.g.* of almandite and fluorite, in Canada balsam, for comparison when making this test.

In the matter of actual measurement of the indices, it is obviously the most accurate procedure to measure both ϵ and ω in uniaxial crystals and α , β and γ in biaxial crystals. This necessitates correct orientations of chosen grains, which must therefore be free to move in the medium selected. Further, observations of birefringence, taking into consideration interference colour-value and thickness as previously described (p. 234), are necessary to assess the lowest and highest indices in terms of optical orientation. It frequently happens, however, that owing to other physical properties, e.g. absence of well-defined cleavage or development of fibrous character, it is difficult, if not impossible, to measure all three indices of a biaxial mineral; in such a case every effort should be made to measure β and thus ensure that the value obtained is neither on the low nor high side. In the case of uniaxial minerals, where positive the *lowest* R.I. is ω and where negative the *highest* R.I. is ω ; this can usually be measured in every instance.

Different authors have proposed various liquids as immersion media according to their requirements and taste. It is possible, of course, to establish a very large range of liquids with refractive indices differing by small increments; for those engaged on very close and detailed work, an extended list is given below; generally speaking, however, those liquids marked with an asterisk(*) will suffice for ordinary work; these have the advantage of chemical stability and if carefully looked after will last indefinitely; they are essentially the liquids adaptable for use under field-conditions and are accordingly recommended. It should be noted that R.I. values may vary with temperature; most of those quoted below refer to 20°C. Where an Abbe refractometer is available, the refractive indices of all liquids employed should be periodically checked.

REFRACTIVE INDEX LIQUIDS

1.333 *Water ¹	1.469 Olive Oil
1.357 *Acetone	1.470 Russian Alboline
1.362 Ethyl Alcohol ²	1.472 *Turpentine
1.381 Ethyl Butyrate	1.474 Liquid Paraffin
1.386 Methyl Butyrate	1.477 American Alboline
1.393 Ethyl Valerate	1.478 Almond Oil
1.407 *Paraldehyde	1.481 *Castor Oil
1.409 Amyl Alcohol ³	1.496 Toluol
1.425 Ethyl Bromide	1.498 Benzol
1.444 *Chloroform	1.500 *Xylol
1.448 Kerosene	1.502 Valvolene ⁴
1.448 Methyl Acetate	1.507 Sandalwood Oil
1.450 *Petroleum	1.516 Cedarwood Oil
1.450 Ethylene Chloride	1.516 Ethyl Iodide
1.460 Lavender Oil	1.525 Ethyl Salicylate
1.463 Carbon Tetrachloride	1.526 Monochlorbenzo

1-531 *Clove Oil ⁵	1-635 α -Monochloronaphthalene
1-535 Cinnamon Oil	1-655 α -Monobromnaphthalene
1-536 Ethylene Bromide	1-700 *Cadmium Borotungstate
1-539 Methyl Salicylate	1-716 Potassium Mercuric Iodide
1-546 *Nitrotoluene	1-737-1-741 *Methylene Iodide ⁶
1-548 Aniseed Oil	1-778 *Methylene Iodide Sulphur Solution
1-550 Bromtoluol	1-868 Methylene Iodide, Sulphur and Iodides ⁷
1-555 *Nitrobenzol	1-68-2-10 Piperine and Iodides ⁸
1-558 Dimethyl Aniline	1-998 (Na line)-2-716 (Li line), Sulphur and Selenium mixtures ⁹
1-561 Monobrombenzol	2-72 (Li line)-3-17 (Li line), Selenium and Arsenic Selenide mixtures ¹⁰
1-570 Benzyl Benzoate	
1-572 Orthotoluidene	
1-586 Aniline	
1-589 Bromoform	
1-600 *Cassia Oil	
1-615 Cinnamic Aldehyde	
1-628 *Carbon Disulphide	

Notes

1, 2, 3 Solvent Action on certain minerals of low R.I.

4 Any clean lubricating (mineral) oil may be used; will not mix with clove oil.

5 R.I. varies from 1-530 to 1-544; will mix with petroleum.

6 Place copper or tin in bottle to prevent discoloration (E.S. Larsen).

7 H. E. Merwin, *Washington Acad. Sci. Journ.*, 3, 1913, p. 35.

8 H. E. Merwin, *loc. cit.* This and the next two compounds are solid at ordinary temperatures; used in a state of fusion. For preparation, see E. S. Larsen, *op. cit.*, and references cited.

9 H. E. Merwin and E. S. Larsen, *Amer. Journ. Sci.*, 34, 1912, p. 47.

10 E. S. Larsen, *op. cit.*, p. 20.

N.B. Solutions of intermediate R.I. can, if required, be obtained by mixing 'limiting' fluids together and testing the product with an Abbe or Tully Refractometer, or with mineral fragments of known R.I.

According to E. S. Larsen, about 80% of known non-opaque minerals falls within the range of R.I. values 1-47 to 1-87. From a purely practical standpoint, the liquids cover this range up to about 1-77, thereafter media solid at ordinary temperatures have to be employed and some of these as 'melts' are not too easy to manipulate. A liquid product known as phenyldi-iodoarsine¹, having a R.I. of 1-743 at 15°C., has been introduced with success and is now generally available.

The best method of storing refractive index liquids is to keep them in 'dropping bottles' supplied with a glass rod fused into the stopper. The bottles are kept in receptacles made by boring holes of suitable size in thick wooden blocks, each block containing ten or twelve bottles, on the principle suggested by E. S. Larsen. *Use coloured glass bottles and keep the liquids tightly stoppered in the dark when not in use.*

¹ B. W. Anderson and C. J. Payne, *Nature*, 133, 1934, p. 66

SUMMARY OF OPTICAL PROPERTIES OF SEDIMENTARY ROCK MINERALS

A good working knowledge of crystallography is essential to understanding the several optical properties used in diagnosis of rock minerals, as hitherto described. The following summary of possibilities will help to bring out the basic differences between such properties as may be anticipated from minerals belonging to the various systems of crystallization and the student would do well to commit the data to memory at an early stage.

1. *Amorphous (Non-crystalline)*. Shapeless grains. No variation in directional properties. *Examples*: Glauconite, limonite.
2. *Isometric (Cubic) System*. Grains are singly refracting, isotropic and never pleochroic. *Examples*: Fluorite, garnet, spinel. Under conditions of internal strain, some species may be anisotropic, e.g. garnet, fluorite.
3. *Hexagonal System*. Grains are doubly refracting and sometimes pleochroic when coloured. Basal grains or those abraded transverse to the hexad axis are isotropic and yield uniaxial interference figures. Prismatic grains give straight extinction. *Example*: Apatite.
4. *Trigonal System*. Grains are doubly refracting and frequently pleochroic when coloured. Basal grains or those abraded at right angles to the principal axis are isotropic and yield uniaxial interference figures. Prismatic grains show straight extinction. *Examples*: Calcite and tourmaline.
5. *Tetragonal System*. Grains are doubly refracting and sometimes pleochroic when coloured. Basal grains or those abraded transverse to the principal axis are isotropic and yield uniaxial interference figures. Straight extinction for prismatic grains. *Examples*: Anatase, cassiterite, rutile, xenotime and zircon.
6. *Orthorhombic System*. Grains are doubly refracting and often pleochroic when coloured. Never completely isotropic. Biaxial interference figures. Prismatic grains show straight extinction. *Examples*: Andalusite, brookite, enstatite and topaz.
7. *Monoclinic System*. Grains are doubly refracting, often pleochroic when coloured. Never isotropic. Biaxial interference figure. Straight or oblique extinction according to crystal plane to which surfaces examined are parallel. *Examples*: Gypsum, orthoclase, epidote and titanite.
8. *Triclinic System*. Grains are doubly refracting and usually pleochroic when coloured. Never isotropic. Biaxial interference figure. Grains usually give oblique extinction, but often fail to extinguish in any position. *Examples*: Kyanite and plagioclase feldspar.

N.B. Exceptionally for grains of biaxial minerals, the crystal-section examined under the microscope may be parallel to the circular section

of the indicatrix. Such grains may show very low interference colours or almost isotropism.

DIFFICULTIES IN IDENTIFICATION OF DETRITAL MINERAL AGGREGATES UNDER THE MICROSCOPE

The petrography of sedimentary rocks is frequently complicated by an inherent difficulty of identifying certain rock-fragments, composite grains (compound minerals), iron-, bitumen- or carbon-stained grains, green or white semi-opaque grains of 'dirty' appearance and a number of other possibilities well appreciated by those who spend much time in searching mineral concentrates under the microscope. The difficulty is accentuated by fineness of grade when, unless exceedingly good illumination and high-power magnification are employed, much of the concentrate may remain obscure; even then, as R. H. Rastall has pointed out¹, 'it is notoriously difficult to apply the ordinary optical tests to very minute grains under a high power, even in the case of transparent minerals, and with opaque grains very little can be done'. With a view to aiding diagnosis in such cases, the following hints from the author's experience may not be without some practical value.

Rock-Fragments. Careful investigation of the coarser constituents of a sediment often reveals large fragments of miscellaneous sedimentary, igneous or metamorphic rocks which may be present as smaller particles in the main mass of the detritus; in this way a clue is obtained and certain types of rock-fragment anticipated. The commonly occurring types range from chert, quartzite, chalcedony, vein-quartz, pegmatite, slate, shale, 'felsite', various igneous rocks, particularly the dark-coloured and usually somewhat altered basic hypabyssal and volcanic types, also mica-schist. As pebbles or large particles, these are not very difficult to determine, especially if cleansed of all cementing matter and examined with a strong lens; thin sections are often possible, even on fragments only 5 mm. in diameter. If, however, the coarse constituents reveal no counterpart of the fragments present in the finer mass, much can be done by observing them in reflected light when the colour, form, surface-characters, lustre, etc., may suggest identity. Normally, unless rock-fragments possess a high iron-content, they will be segregated by the bromoform-benzol solution or later by bromoform itself in the process of routine separation previously described, so that they should not interfere greatly with the heavy mineral suite.

Composite Aggregates (Compound Grains). Attachment of iron-ore to quartz, mica to quartz, rutile to ilmenite, pyrite to chert and such compound minerals as leucoxene, perthitic intergrowths of feldspar, mica-chlorite aggregates, shimmer aggregates, etc., are frequent occurrences in sediments and their diagnosis may occasionally be troublesome.

¹ *Geol. Mag.*, 60, 1923, p. 37.

The compound *iron-ore-quartz* grain should betray its nature by its behaviour with polarized light, when characteristic concentric interference colours of quartz are normally visible and contrast with the opaque portion identified with reflected light.

Mica-quartz grains are less common, but the two minerals can usually be differentiated by their slight difference of refractive index (mica having the higher value) tested by the Becke line method; the mica portion also will usually show a complete interference figure, while if the concentric coloured rings of quartz are discerned, this property will contrast with the pale grey-blue or grey-yellow colour of the mica; failing this, reflected light will reveal the vitreous lustre of the quartz and the pearly lustre of the mica, usually a sharp contrast.

Compound ilmenite-rutile or ilmenite-anatase grains are generally straightforward to diagnose, the secondary crystals of the oxides being conspicuous by their colours, refractive indices and euhedrism. Cases have been noted, however, where the co-existence of the ilmenite-rutile aggregate can only be inferred by inspection of the grain by reflected light, when a reddish or crimson patch or border, contrasting with the steel-grey lustre of the unaltered ilmenite, is visible. This characteristic may, however, be noted with certain types of ilmenite in which there is no reason to suspect decomposition and generation of rutile.

Chert as a matrix or nucleus in composite grains is not uncommon, but should be readily identified by its aggregate polarization; *pyrite* attached to it may be fresh or altered to limonite, in either case recognized by reflected light; pyrite as a core is usually fresh and gives no trouble in identification.

Leucoxene is a much debated substance, but one which is not difficult to label, owing to its characteristic appearance by incident light; according to A. Cathrein¹ this product is essentially titanite, sometimes accompanied by rutile; it has, however, a very different appearance from titanite and in fact shows every variation from the partially-altered ilmenite grain, through limonite or hematite-stained aggregates to the uniform white 'unglazed porcelain' type of grain familiar to all workers.

Perthitic Intergrowths of Felspar are identifiable, providing the grains are not clouded with kaolinitic or micaceous material, when the optical characters are discernible with polarized light; if microcline enters into the composition of such aggregates, the 'partial' cross-hatching is always suggestive; if compounded of orthoclase and plagioclase, diagnosis is often difficult, especially with small grains.

'*Chlorite*' aggregates with or without mica are common in certain types of sediment, especially those derived from basic and ultrabasic rocks. Such aggregates are not always easy to decipher, though the bright 'ultra blue' polarization patches of the chloritic minerals contrast with the more vivid coloured mica flakes if these components are individually distinctive; often the aggregate may be a complex product

¹ *Zeitschr. Kryst. Min.*, 6, 1882, p. 244.

resulting from decomposition of some aluminous silicate, when the components lose their individuality as definite minerals and reveal themselves in the form of bluish-yellow birefringent grains possessing no particular extinction direction or other property aiding diagnosis; such grains frequently have a curious rough matted surface by reflected light and this feature is sometimes helpful.

Shimmer-Aggregates result from the decomposition of aluminous silicates and usually consist of felted, cryptocrystalline, white micaceous material often crowded with inclusions. These interesting grains are very variable in form and optical character, often possessing no particular directional properties. The interference colours are normally high. By reflected light the felted structure is accentuated and the lustre is that of a semi-vitreous or porcellaneous character. G. Barrow has described aggregates of this type with cores of staurolite¹; H. H. Thomas also records their occurrence in the Bunter Pebble Beds of the West of England.²

Pinite is another aggregate, sometimes mineralogically distinctive, but generally of a micro- to crypto-crystalline character, rather micaceous, green in colour and intimately associated with iron-ore; it usually results from the decomposition of cordierite.

Hematite, either as an isolated mineral or as part of a composite grain, is seldom difficult of recognition on account of its characteristic red colour. If there is any doubt, however, the interposition of a green glass between the source of light and the aggregate (against a grey background) or use of a green electric lamp may prove helpful; in these circumstances hematite appears dull black.

USE OF COLOURED LIGHT IN PETROGRAPHIC WORK

Coloured light as an aid to petrographic work is not perhaps as freely invoked as it might be, either for transmitted or incident light observations. In practically all the instances cited, coloured electric lamps of sufficient strength or the employment of suitable filters made of different coloured glass, may sometimes prove advantageous. The following colours have been successfully employed by the author in this connexion:

Red for chloritic matter, glauconite, epidote, green mica aggregates.
Green for hematite.

Blue for limonite (especially limonitic patches on glauconite).

Yellow for any aggregate in which either purple ilmenite or pyrolusite is anticipated.

The effect in each case is to make the particular mineral components appear nearly black or quite dull, thus contrasting better with the associated minerals, especially if the latter are transparent

¹ *Quart. Journ. Geol. Soc.*, **49**, 1893, p. 349 and Pl. 16, Fig. 5.

² *Quart. Journ. Geol. Soc.*, **58**, 1902, p. 627.

or light coloured; such illumination enables the form of the chloritic matter, hematite, etc., to be picked out more easily.

MINERALS MASKED BY ALTERATION PRODUCTS

The determination of minerals possessing superficial decomposition products, unremoved by the usual methods of clarification, is a well-known difficulty in work with detrital sediments. The cerium oxide film on monazite; opaque green-black dust observed as coating to the commoner pyroxenes and epidote; chloritic alterations of ferro-magnesian minerals; carbonaceous matter associated with andalusite; various masks assumed by carbonate minerals: all these are common examples of destabilization products which serve to hide the true character of the original mineral. Sometimes the product may be diagnosed after careful inspection by incident light, whence the fundamental mineral or existing nucleus may be inferred. Use of high power objective with convergent light frequently affords sufficient transparency for such deductions to be made with some accuracy; even optical determinations may be possible in these circumstances. On the other hand, the decomposition film is often so thick and comprehensive that the microscope is powerless to resolve it, let alone the primary mineral concerned, in which case experience and intuitive deduction will be the safest guide. In point of fact, it is with these alteration products as with individual detrital grains: often the experienced investigator can be reasonably certain of his diagnosis without being very clear why his conclusions should impress themselves so decidedly on his mind. Perhaps this is one of the psychological peculiarities of this branch of petrographic work, but it is none the less a generally admitted fact.

Against all this and purely as a temporary expedient when comparing mineral assemblages, the labelling of an unknown species as 'X', while technically indefensible, may suffice until such time as more extended facilities are at hand for a thorough investigation. The recognition of 'X' in a series of samples, providing it has constant mineralogical characteristics, may be of definite index value. While the author in no sense upholds 'makeshift' practice, it behoves him none the less to mention at least one way of overcoming a difficulty so that when petrographic methods of correlation are invoked they may proceed without serious interruption arising from ignorance of specific identity.

In cases where every microscopical and other device fails to give a clue to identity, then there is nothing else for it but to hand-pick under the microscope sufficient grains of the unknown (providing it is not an isolated or rare occurrence) and submit them to chemical

analysis or other tests. This often implies treatment of a large quantity of raw material to produce at least 0.5 g. of the mineral concerned. With isolated grains, the diagnosis of which is essential, spectrographic methods would appear to offer the only solution (Chapter XI).

CHAPTER VII

METHODS OF TESTING SEDIMENTARY ROCKS¹

Introduction - Acid Solubility - Aggregates - Aggregate Crushing Value - Bitumen Content - Bulk Density of Coarse and Fine Aggregate - Bulk Density of Filler in Benzene - Clay, Fine Silt and Fine Dust Content in Fine or Coarse Aggregates - Cohesiveness of Sands - Density - Elongation Index - Flakiness Index - Frequency Factor - Grain Size - Gravel Constituents - Hardness - Heavy Mineral Content - Micrometric Analysis - Moisture Content (Hygroscopic) of Sediments - Moisture Content (Hygroscopic) of Asphalt and Bituminous Impregnated Rocks - Organic Impurities - Permeability - Petrological Examination for Nature of Components - Planimetric Analysis - Point Counter Porosity - Reactive Components in Gravel Aggregates used in Concrete - Roundness - Shape - Sieve Analysis - Specific Gravity - Specific Surface - Sphericity - Surface Texture (Textural Analysis) - Void Content of Dry Compacted Filler - Voids - Volume Weight (or Weight per Cubic Foot) - Water Absorption Weight per Cubic Foot.

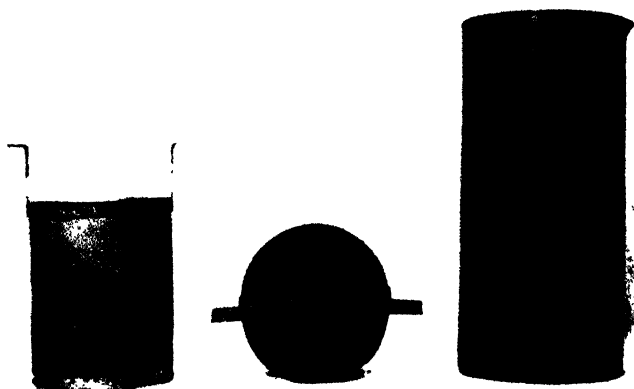
INTRODUCTION

IN this chapter are given detailed descriptions of some of the more important laboratory methods of test now in vogue for determining specific properties and characteristics of sediments. Excluded here are principles of mechanical analysis and optical methods to which Chapters IV and VI respectively are devoted.

A universal desire to introduce the quantitative element more freely into petrographic work has in recent years found expression not only in academic spheres of study, but perhaps more forcibly in industrial applications, where standardization of raw sedimentary materials or uniformity of definition of certain outstanding characteristics, is essential to their utilization.

Much purely petrographical investigation is perforce qualitative; it depends rather on description than on any degree of mathematical

¹ In the 3rd edition (1940), this Chapter was written by L. J. Chalk, M.Sc., F.R.I.C., F.Inst.Pet., formerly Chief Chemist, Geochemical Laboratories. It has now been revised, extended and brought up to date by A. H. Clarke, M.Sc., F.R.I.C., A.F.Inst.Pet., Chief Chemist, Geochemical Laboratories and the author.



A. GAUZE BASKET, CONDENSER COIL AND ALUMINIUM BEAKER.
(*Geochem. Labs.*)



B. GALLENKAMP CENTRIFUGE.
(*Courtesy A. Gallenkamp & Co. Ltd., London, E.C.2.*)

exactitude in defining appropriate characteristics of sedimentary rocks. On the other hand, most rock-types are capable of yielding indicative quantitative data, enabling more precise comparisons and contrasts to be made and the more this aspect of the science is developed, the more thorough is our understanding of the materials involved.

The last two decades have witnessed a great advance in methods of testing sedimentary rocks and minerals. Essential criteria for a generally acceptable method of test are that (a) conditions of test, (b) apparatus employed, (c) manipulation, (d) permissible tolerances and (e) interpretation of results, should all be specified so clearly that independent workers on identical samples are in a position to achieve reproducible results. Only on such a basis are comparisons really worth anything.

Petrographic methods as generally known, apart from particular national or international standards as to procedure, lack uniformity, also any substantial measure of agreement as to what constitutes the most accurate and unequivocal method of conducting a particular test. This is largely born of multiplicity of independent efforts without any real (and subsequent) co-ordinating plan. Attempts have been made, not without some success, to standardize petrological nomenclature, but the same cannot as yet be said of processes of investigation of sediments and much remains to be done in this connexion. Fortunately industry has given a lead in certain directions and the following descriptions of some of the commoner determinations made with sedimentary rocks, will enable the student to introduce a degree of precision and standardization into the technique of his work.

The tests described in this Chapter are arranged in alphabetical order.

ACID SOLUBILITY

The acid solubility of a sediment is that proportion which is soluble in hydrochloric acid of a prescribed strength under certain specific conditions. A high acid solubility usually, but not always, implies presence of organic rocks such as limestone, chalk, ragstone, etc. The determination is useful for comparing samples of calcareous rocks from different horizons or localities and for expressing their degree of purity or contamination by detrital and/or authigenic constituents. The method recommended for sediments is similar to that originally described in B.S. 598 : 1936¹ and is as follows:

¹ Sampling and Examination of Bituminous Road Mixtures. This method has been omitted from later editions of this Standard, but it is still, in principle, followed in the author's laboratories.

The sample is crushed to pass a 52 mesh B.S. sieve and 5 g. weighed into a 300 ml. beaker. 25 ml. of 6N hydrochloric acid are added and allowed to stand covered with a watch glass for a quarter of an hour or until effervescence has ceased. The addition of a few drops of alcohol to the powder before the acid, accelerates the reaction. 200 ml. of distilled water are then added, the whole boiled and decanted through a filter paper, which has been previously dried and weighed in a weighing bottle. The residue in the beaker is washed twice with cold dilute hydrochloric acid and then several times with hot distilled water and the total contents of the beaker transferred to the filter paper and washed with hot water until the filtrate is free from acid. The residue is dried at 110°C. to constant weight and is calculated as a percentage by weight of the original sample taken. The difference between 100% and the value obtained is the percentage solubility of the rock. The moisture content (p. 274) need be determined only if there is reason to suspect the presence of an appreciable amount of hygroscopic water. In this case the percentage of moisture found is deducted from the acid solubility as determined above.

AGGREGATES

For purposes of testing, a mineral aggregate is defined as 'Aggregate consisting of naturally occurring rock, gravel or sand or of artificially produced inorganic materials'¹. In other words, any mechanically crushed rock, coarse to fine in grade-size; any naturally occurring gravel, sand, similarly coarse to fine in grade size, apart from synthetic materials, may constitute objects of laboratory examination for specific constructional or industrial requirements.

The following acceptance tests are commonly applicable to aggregates used in building, highway and runway construction (concrete, mortar, asphalt, tarmacadam, etc.); they may be suitably employed in other circumstances where incoherent materials are involved:

Acid Solubility (p. 257)

Aggregate Crushing Value (p. 259)

Bulk Density (p. 265)

Clay, Fine Silt or Dust Content (p. 267)

Elongation Index (p. 269)

Flakiness Index (p. 270)

Moisture Content (p. 274) :

Organic Impurities (p. 275) :

Petrological Examination for Nature of Components (p. 278).

Reactivity (Potential Alkali Reactivity to Hydration of Portland Cement) (p. 288)

Shape (p. 290)

Sieve Analysis (p. 292)

Specific Gravity (p. 292)

¹ B.S. 812 : 1951, Sampling and Testing Mineral Aggregates, Sands and Fillers, clause 2b, p. 8 (Revised 1960).

Surface Texture (Textural Analysis) (p. 296)

Voids (p. 297)

Water Absorption (p. 297)

The methods involved in the above tests are essentially those performed in the author's laboratories and in most cases follow standard procedure as laid down in B.S. 812 : 1960.

In addition to the above, there are certain mechanical tests which, apart from Aggregate Crushing Value, are carried out on aggregates for special purposes, *e.g.* aggregate impact value, crushing strength (of component rocks), resistance to wear by abrasion and attrition; these are not described here and reference should be made to the appropriate British Standard¹ for full details.

AGGREGATE CRUSHING VALUE

This is a particularly useful test in classifying or sorting aggregates destined for use in concrete or asphalt mixtures. The standard test is carried out on $\frac{1}{2}$ in. – $\frac{3}{8}$ in. aggregate, but other sizes can be accommodated (see table below). The test is made in duplicate and mean of two results is reported. Procedure is as follows:

From the bulk (56 lb., $\frac{3}{8}$ in. or smaller, 2 cwt. + $\frac{3}{8}$ in.) segregate minimum 14 lb. if practicable of $\frac{1}{2}$ in. – $\frac{3}{8}$ in. fraction; dry for 4 hours at 100°–110°C. Cool. Weigh. A cylindrical metal measure 4½ in. diameter and 7 in. high (internal) is filled $\frac{1}{3}$ rd full with the aggregate and tamped down 25 times with a straight metal rod of circular cross-section, $\frac{5}{8}$ in. diameter, 24 in. long, bullet-nosed at one end. A further $\frac{1}{3}$ rd quantity of aggregate is next added, then 25 more strokes with the tamping rod are given. Now fill the measure full to overflowing, give 25 more strokes and then level off any surplus with the rod. Determine net weight of the sample thus prepared; this weight is used for duplicate test on the same material.

The test apparatus consists of an open-ended steel cylinder, 6½ in. internal diameter, with wall not less than $\frac{5}{8}$ in. thick, height 5½ in., mounted on $\frac{1}{2}$ in. thick base-plate 9 in. square. The interior surfaces in the cylinder must be case-hardened with diamond pyramid hardness value 650. A hardened plunger 1 in. thick, 6 in. diameter, 4 in. high (4½ in. diameter across flat top), is fitted with $\frac{1}{2}$ in. pipe which passes through two holes on either side (centred 3 in. above base of plunger) serving as lifting handle, completes this equipment.

Test procedure is to fill cylinder in thirds, giving each third 25 strokes with tamping rod. Level surface of aggregate, insert plunger, remove lifting handles; place the whole apparatus in a compression testing machine and apply a load of 40 tons at a uniform rate of 4 tons per minute. When the load is released, all the aggregate is taken out of the cylinder and sieved on a 7 B.S. sieve. The material passing that sieve is weighed.

¹ B.S. 812 : 1960.

Ratio of weight of —7 B.S. material to total weight of sample taken is expressed as percentage (to first decimal place). The process is repeated on the counterpart sample and mean of the results of the two is the aggregate crushing value of the material tested.

The following table gives details of this test for non-standard sizes of aggregates. It is generally found that larger sizes give higher and smaller sizes, lower aggregate crushing values than standard-size material.

TABLE 4
DETAILS OF AGGREGATE CRUSHING TESTS FOR
NON-STANDARD SIZES OF AGGREGATE¹

Nominal size of aggregate		Dia- meter of cylinder to be used	Approximate quantity of material to provide two test samples		Depth of sample in cylinder after tamping	Total load	Size of B.S. sieve for separating fines	
Passing	Retained							
in.	in.	in.	lb.	kg.	cu. ft.	in.	tons	in.
2	1½	12	112	50	1	8	160	¾
1½	1	12	112	50	1	8	160	¾
1	¾	12	112	50	1	8	160	¾
¾	½	6	14	6·5	½	4	40	¾
¾	¾	6	14	6·5	½	4	40	No. 10 No. 14 No. 18
¾	⅝	3	2	0·8	⅝	2	10	
⅝	⅝	3	2	0·8	⅝	2	10	
½	No. 7	3	2	0·8	⅝	2	10	No. 25

In interpreting results, the lower the percentage of —7 B.S. material on test, the better the toughness, mechanical strength and durability of aggregate. The value should not exceed 25% with standard ½ in. material used in asphalt. Maximum aggregate crushing values for concrete are 30% for wearing surface and for other purposes 45% which, in the author's opinion is unduly high². Normal flint and quartzite gravels, for example, may be expected to reveal values (½ in.) between 10% and 18%; chert ranges between 15%–20%; limestone aggregates tend to higher crushing values, 20%–25%, but normal Carboniferous (especially dolomitic) varieties may give lower values than 20%. Slag aggregates vary greatly; only the hard, dense, crystalline varieties stand up to this test and

¹ B.S. 812 : 1951, Table II, p. 49. (Revised 1960).

² B.S. 882 : 1954, Concrete Aggregates from Natural Sources, clause 3c, p. 6.

the value is usually between 25%-30%; porous, honeycombed slag produces very high values. For further detailed information on this test, references below should be consulted¹.

BITUMEN CONTENT

Oil-saturated sands containing fluid hydrocarbons may be clarified by repeated digestions of the sample with benzol, chloroform, ether, carbon disulphide or trichloroethylene. If, however, impregnation is of a solid asphaltic character, an extraction process must be carried out. For this purpose it is preferable to take such a quantity of sample (minimum 100 g.) as will give an adequate amount of mineral matter for preparation of slides for petrographic study. The method of D. M. Wilson² will be found to be a convenient process to use; it is known as the 'funnel' method and is a standard³; alternatively, the following method, which differs from it only in certain minor manipulative details, may be employed.

The sample is reduced by the usual crushing and quartering procedure (p. 71) until two portions approximately 100 g. in weight are obtained. These are then ground as finely as practicable and dried in the oven for two hours at 105°C. It is important to note that samples for precise soluble bitumen determinations should be dry or alternatively the moisture content of the rock should be determined on an aliquot portion of the sample by the method given on p. 274. It will be found that rocks containing low percentages of impregnated bitumen can be ground far more readily than highly impregnated specimens, which tend to cake during the grinding process.

Two Whatman No. 5 filter papers, 32 cm. in diameter, are examined for pin holes by holding to the light; if satisfactory they are marked with an identifying number and dried in an oven at 105°C for two hours, after which they are quickly transferred to weighing bottles and placed in a desiccator. Dry filter papers absorb moisture from the atmosphere extremely quickly and the transference should therefore be made rapidly. When weighed, the filter papers are folded in the manner

¹ *Concrete Roads*, D.S.I.R., Road Research Laboratory, 1955, pp. 22, 23 and Pl. 2.2.

F. A. Shergold, *A Review of Available Information on the Significance of Roadstone Tests*, D.S.I.R., Road Research Technical Paper No. 10, 1948.

F. A. Shergold, *The Testing and Use of Gravel for Road Construction, Cement, Lime and Gravel*, 22, 1947, pp. 62-66.

A.S.T.M. Standards, Part 3, Concrete, Road Materials, etc., 1952 (Tests on Aggregates).

B.S. 812 : 1960, Methods for the Sampling and Testing of Mineral Aggregates, Sands and Fillers.

² *Journ. Soc. Chem. Ind.*, 50, 1931, p. 600.

³ B.S. 598 : 1958, Sampling and Examination of Bituminous Road Mixtures, Method A, p. 16.

shown (Fig. 34) and fastened with paper clips, after which they are placed in 8 in. glass funnels, the top edges of which have been ground flat on a carborundum plate.

The weighed sample is carefully introduced into the filter paper and a circular glass plate 9 in. diameter, with a hole $\frac{3}{8}$ in. in diameter in the centre, placed over the top. If desired the plate may be sealed to the funnel, using a cement consisting of:

Gelatine	10g.
Water	80 ml.
Glycerine	20 ml.

One crystal of phenol added to this quantity of cement will prevent the growth of moulds. The cement can easily be remelted on a water bath and is painted on the funnel rim while hot, care being taken to prevent it running down on the inside of the funnel.

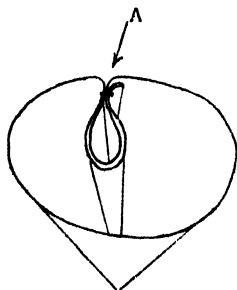


FIG. 34. Method of folding Filter paper for Bitumen extraction. A --- position of paper clip. (After B.S. 598, 1958, Fig. 1).

A 3 in. funnel is then placed in the hole in the centre of the plate, with its stem inside the 'loop' of the filter paper and trichloroethylene or carbon disulphide added until the level of the solvent is $\frac{1}{2}$ in. below the top of the filter paper. The solvent passing through the filter paper is collected in large bottles and returned to a 5 gallon drum for re-distillation and recovery at a convenient opportunity.

The funnels are re-filled (at intervals) and the level of the solvent kept as high as possible throughout the filtration. On no account should they be allowed to run dry.

When the filtrate is a very pale straw colour (it is never actually colourless within a reasonable period of time), extraction is considered to be complete and the filter paper is allowed to drain. It is then placed on the top of an oven until most of the solvent has evaporated, after which the paper clip is removed, the paper carefully opened and placed inside the oven. If carbon disulphide has been employed as the solvent, the paper should not be placed near a source of heat as long as the odour is very apparent, or it may catch fire. After one hour at 105°C., the paper is removed and the mineral matter scraped from it with the aid of an ordinary nickel spatula and transferred to a previously dried and weighed beaker, which is then returned to the oven and dried to constant weight. The filter paper is also dried for a further hour, after which it is quickly replaced in its original weighing bottle and weighed. The difference between the weight of the original sample and the weight of residue left after extraction gives the amount of soluble bitumen.

Geochemical Laboratories Rapid Method for Determination of Soluble Bitumen

This method is based on one devised originally by L. J. Chalk¹. It is applicable to analysis of bituminous mixtures containing less than 20% of material passing a 200 mesh B.S. sieve. It is not suitable for analysis of mastic asphalt. The apparatus described has been in use for several years in these Laboratories and is of a convenient size for most work. Exact dimensions are not, however, critical.

The extractor consists of an aluminium beaker, 6 in. diameter and 12 in. high, in which is suspended a cylindrical basket, 5 in. diameter and 6 in. high, constructed from 100 mesh gauze. A condenser, made from a spiral of $\frac{1}{4}$ in. diameter lead compo tubing, fits into the top of the beaker (Fig. 35, also Pl. 9A). A centrifuge is also required; the type used in these Laboratories has a maximum speed of 5,000 r.p.m. and a capacity of four 100 ml. tubes (Pl. 9B). To avoid breakages, aluminium tubes are used.

Soluble bitumen determinations are carried out in duplicate and 500 g. portions of sample are taken in the case of sand carpets. For other types of material the weights taken are in accordance with B.S. 598 : 1958, Table 3. It should be noted that when portions of 5 kg. are required, it is necessary, with this apparatus, to use several baskets to accommodate the sample. If a considerable amount of work on material of this type is undertaken, it is desirable to employ larger beakers and baskets.

The asphalt sample is prepared for analysis in accordance with B.S. 598 : 1958, Method A. The basket is weighed (*A*); a suitable quantity of material to be tested is placed in the basket and the whole re-weighed (*B*).

Approximately 300 ml. of trichloroethylene is placed in the beaker and the basket suspended 3 in. above the surface of the liquid. The condenser coil is placed in position and the beaker heated so that the solvent condenses on the coil. The time required for complete extraction of the bitumen varies with the type of material analysed. Extraction is usually complete in about 2 hours. After allowing to cool, the basket is removed and dried to constant weight (*C*) in an oven at 105°–110°C.

The bitumen solution and mineral matter in the beaker are transferred completely to centrifuge tubes and centrifuged for a minimum time of 5 minutes at 3,000 r.p.m. The liquid is decanted and the mineral matter in the tubes stirred with clean solvent. After centrifuging as before, the liquid is again decanted and the washing procedure repeated, if necessary. The clean mineral matter is dried and weighed (*D*) and added to the extracted material in the basket for sieve analysis.

$$\left. \begin{array}{l} \text{Soluble bitumen} \\ + \text{water \%} \end{array} \right\} = \frac{B - (C + D) \times 100}{B - A}$$

¹ *Journ. Inst. Pet.*, 25, 1939, p. 168.

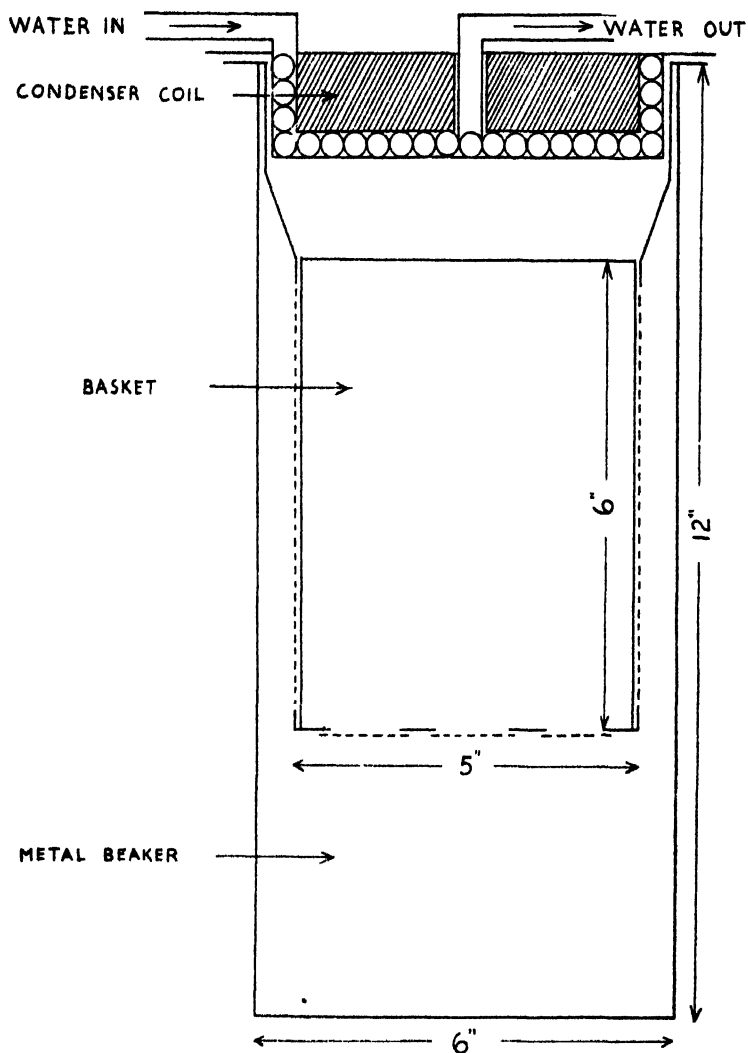


FIG. 35. Diagram of apparatus for rapid method of determining soluble bitumen (Geochemical Laboratories).

If the material contains water, it is necessary to carry out a separate water determination.

The results obtained by the above method are in excellent agreement with those obtained by the standard Wilson ('funnel') method, even when the sample contains Trinidad Lake Asphalt.

I.P. Methods¹

For bitumen content of various types of asphalt, standard I.P. methods are available according to the nature of the material to be analysed. Six methods, A, B, C, D, E and F are laid down; they are all technically equivalent to those described in B.S. 598: 1958, Part 3. Method A is the 'funnel' method as described above, applicable to all bitumens and bituminous mixtures. Method B is a centrifuge method applicable to all types of asphalt excepting samples anticipated to contain 50%–95% of bitumen. Method C is an extraction bottle method, applicable to natural rock asphalt, hot rolled asphalt, fine cold asphalt and bitumen macadam. Method D is a sieving extractor (methylene chloride) method, developed at the Road Research Laboratory (D.S.I.R.), applicable to the same mixtures as Method C. Method E is a simple hot extractor method applicable to fine cold asphalt and bitumen macadam, while Method F is a compound hot extractor method with similar applications as Method E. For native bitumens and bituminous materials containing more than 95% of bitumen, the method involving solubility in carbon disulphide (I.P.47/58) is laid down. Full details of all these methods are given in the I.P. (1958) volume referred to below.

Methods of determining soluble bitumen content are constantly under critical review both for B.S. and I.P. purposes, but the 'funnel' method (A) is standard 'referee' procedure and is always adopted in cases of dispute or doubt.

BULK DENSITY OF COARSE AND FINE AGGREGATE

The density of a substance is the ratio of its mass to its volume (mass per unit volume). It is a determination frequently required for gravel aggregates and sands for concrete etc. The test is normally made on oven-dried material but it may also be carried out 'as received', often saturated and surface-dry; or the moisture content may be predetermined and a correction made accordingly. The method described below is one of direct measurement and is based on the British Standard test for bulk density².

¹ *Standard Methods for Testing Petroleum and its Products*, Institute of Petroleum, 17th ed., 1958, I.P. 162/58, p. 45.

² B.S. 812 : 1960, clause 25.

A cylindrical metal container of varying dimensions according to nominal size of aggregate to be tested (see table below¹), is first calibrated by filling with water at 20°C. and determining weight of that water, W_1 (lb.).

TABLE 5
SIZE OF CONTAINER FOR BULK DENSITY TEST

Size of largest particles	Nominal capacity	Internal diameter	Internal depth	Minimum thickness of metal	
in.	cu. ft.	in.	in.	S.W.G.	in.
Under $\frac{1}{16}$	$\frac{1}{16}$	6	6	11	0.116
From $\frac{1}{16}$ to $1\frac{1}{2}$	$\frac{1}{8}$	10	11	8	0.160
Over $1\frac{1}{2}$	1	14	11 $\frac{1}{4}$	5	0.212

Volume of container is given by:

$$\frac{W_1}{W_2}$$

where W_1 = weight of 1 cu. ft. of water at 20° C. (62.4 lb.).

Where loose weight is required, fill container to overflowing from a height not exceeding 2 in. above its top. Level off with straight edge. Where rodded or compacted weight is required, fill container one-third full and tamp down 25 times with tamping rod 2 ft. long, $\frac{3}{8}$ in. diameter, with bullet-nosed end; add another third of aggregate to container and tamp again 25 times; finally fill container to overflowing, tamp again 25 times and strike off surplus with tamping rod. In either procedure determine net weight of aggregate in container, hence calculate bulk density in lb./cu. ft.

BULK DENSITY OF FILLER IN BENZENE

In certain specifications, where some idea of surface-area of fine aggregate (—200 material) is wanted², this test is indicative and has been standardized for the purpose³. Procedure is as follows:

Dry a sample of the filler for 4 hours in a ventilated oven at 105°–110°C., then cool in desiccator to room temperature. Take 10 g. of sample (weighed to ± 0.01 g.) and place in 50 ml. measuring cylinder (glass stoppered), 19 cm. long, 2.2–2.5 cm. internal diameter, calibrated in millilitres. Half fill cylinder with pure benzene⁴; replace stopper; shake until sample is completely wetted. Then add more benzene to bring level within 4 cm. from top of cylinder. Shake again. After this, invert cylinder to allow air bubbles to travel through the suspension;

¹ B.S. 812 : 1951, Table 10. (Revised 1960).

² B.S. 594 : 1958, Rolled Asphalt (Hot Process), Table 4.

³ B.S. 812 : 1951, clause 20. (Revised 1960).

⁴ Dried over calcium chloride for 24 hours.

return to upright position and allow air bubbles to travel back. Repeat this inversion and return process 5 times in rapid succession and then place cylinder on firm surface and leave for at least 6 hours. Bulk volume (V) is then read off from the graduations. The test is made in triplicate, using separate samples of filler each time and mean value of three results reported to the nearest 0.1 g./ml.

$$\text{Bulk density} = \frac{10}{V} \text{ g./ml.}$$

B.S. 812 stipulates that if any of the three values as obtained above differs by more than 0.05 g./ml., from mean value, the result shall be discarded and two further re-tests carried out. For fillers used in asphalt, bulk density in benzene is usually within the range 0.50 g.-0.95 g./ml.

CLAY, FINE SILT AND FINE DUST CONTENT IN FINE OR COARSE AGGREGATES

Two methods are in general use, one known as the Field Settling Test, the other as the Sedimentation Method. The former is a fairly rapid method and gives but a rough idea of clay and silt content in the aggregate. The latter constitutes a more accurate laboratory procedure. Both are applicable in certain aspects of petrographic work.

For *Field Test*, a 200 ml. graduated measuring cylinder¹ containing about 50 ml. 1% salt solution is used. The sample is added to the cylinder until volume of sandy layer reaches 100 ml. Salt solution is then added until volume is made up to 150 ml. Covering mouth of the cylinder, shake vigorously, then allow to stand for 3 hours. Height of silt-clay layer above aggregate below it is expressed as percentage of that aggregate².

*Sedimentation Method*³ involves use of a sedimentation pipette of Andreason or similar type (see Chapter IV, p. 158). Procedure is as follows. Initially weight of sample required depends on nominal size of largest particle present and is thus laid down⁴:

$\frac{3}{16}$ in.	0.250 kg.
$\frac{1}{4}$ – $\frac{3}{8}$ in.	0.500 kg.
$\frac{1}{2}$ – $\frac{3}{4}$ in.	1 kg.
$1\frac{1}{2}$ – $2\frac{1}{2}$ in.	6 kg.

For — $\frac{3}{8}$ in. fine aggregate, dry, weigh and place in glass stoppered jar (2 lb. fruit preserving type is suitable) in which there are 300 ml. sodium oxalate solution (0.8 g./litre). Ensure that stopper or cap is secure.

¹ B.S. 604 1952.

² B.S. 812 1951, clause 14, p. 26.

³ B.S. 812 1951, clause 12, p. 21. } (Revised 1960).

⁴ B.S. 812 1951, Table 7.

Place jar in a rotating machine (80 ± 20 r.p.m.) in horizontal position and rotate for 15 minutes. Then transfer contents of jar to 1000 ml. measuring cylinder, washing out stray sediment by swirling and decantation of successive 150 ml. portions of sodium oxalate solution, until all washings make up volume to 1000 ml. Invert cylinder (duly covered) and then replace in upright position under the pipette apparatus. Volume of pipette must be pre-determined.

The pipette is next lowered 10 cm. into the solution; after 3 minutes, by gentle suction, it is filled to appropriate mark. The pipette (closed) is then removed from the measuring cylinder and its contents transferred to a weighed container, dried at 110°C to constant weight, cooled and weighed.

Percentage of clay, fine silt or fine dust is given by:

$$\frac{100}{W_1} \left(\frac{1000W_2}{v} - 0.8 \right)$$

where W_1 = weight of original sample (g.); W_2 = weight of dried residue (g.); v = volume of pipette (ml.); 0.8 = weight of sodium oxalate in g. in 1000 ml. of diluted solution.

With material $\frac{1}{8}$ in. (coarse aggregate), procedure is much the same. Weigh the sample, place in container, cover with known volume of sodium oxalate solution (0.8 g./litre), agitate to remove fine material and transfer final liquid suspension to 1000 ml. measuring cylinder. Repeat procedure until all clayey matter has been removed from original sample and make up to 1000 ml. with sodium oxalate solution. Then proceed with pipette apparatus, measurements and calculations as above.

COHESIVENESS OF SANDS

This test is used to determine relative cohesiveness of different sands and as an indication of the amount of water which will develop optimum cohesiveness (equivalent to 'bonding' tests in foundry practice). The simplest method is that known as the 'Bar Test' fully described by R. J. Doty¹, and later by H. Ries and C. M. Nevin². It consists in ramming a known quantity of sand in a mould-box with a 20 lb. weight dropped between two guides from a height of 16 in., six blows being given per test. The data required and obtained by this test include weight of sample in grams, thickness of bar in inches, average weight of break in grams and recalculated weight of break to 1 in. thickness; correction for water content necessitates knowing the percentage of water with which the sample is gauged and recalculating weight of break to a dry sand basis, with which data all cohesiveness tests should be compared³.

¹ *Foundry*, 51, 1923, p. 15.

² *Trans. Amer. Found. Assoc.*, 31, 1924.

³ See also relevant papers in *Trans. Amer. Found. Assoc.*, 32, 1925.

DENSITY

The density of a substance is the ratio of its mass to its volume (mass per unit volume). In C.G.S. system, it is expressed as grams per millilitre and in F.P.S. system as pounds per cubic foot. In precision work the temperature of determination of density must be recorded.

If the temperature at which the determination is carried out is 4°C., density in C.G.S. units is numerically equal to sp.gr., *i.e.* mass of a given volume of a substance compared with mass of an equal volume of water. The mass of a cubic foot of water at 4°C. is 62.4 lb., hence in F.P.S. units density at 4°C. divided by 62.4 will be equal to sp.gr. of the substance at that temperature. Following the lead given by the British Standards Institution¹, use of density at 20°C. in preference to specific gravity at 15.5°C., is now becoming increasingly common in industry.

The general formula connecting density and specific gravity is as follows:

$$D_t = \text{s.g.}_t \times d_t$$

where D_t = density of substance at t° ,

s.g._t = specific gravity of substance at t° , compared with water at t° ,

d_t = density of water at t° .

See also under Bulk Density of Coarse and Fine Aggregate (p. 265); Bulk Density in Benzene (p. 266) and Specific Gravity (p. 292).

ELONGATION INDEX

Apart from usual qualitative expressions of particle shape (p. 290) in petrographic work, there are two functions often measured in mineral aggregates destined for constructional materials, *viz.*, elongation and flakiness (p. 270) indices. These determinations are not always sought together, hence their separation here.

Elongation index as applied to aggregate constituents, whatever nominal size of material under test, means 'the total weight of the material retained on the various length gauges, expressed as a percentage of the total weight of the sample tested'². The standard length gauge is a device which enables direct measurements to be made of aggregates of various nominal sizes from -2 in. to +1¼ in. B.S. sieves³. Gauge lengths are in proportion to aggregate size and are equal to 1.8 times the mean sieve size of the aggregate tested.

¹ B.S. 733 : 1952, Density Bottles.

² B.S. 812 : 1951, clause 15g, p. 30. (Revised 1960).

³ *Ibid.*, Fig. 8, p. 29.

When using the gauge, sieve analysis of the aggregate is first carried out, the sample is weighed, and then procedure is governed by the following data¹:

Size of aggregate (B.S. sieves)	Length gauge	Minimum no. of pieces to be tested
in.	in.	
-2 + 1½	3.15	300
-1½ + 1	2.25	300
-1 + ¾	1.57	200
-¾ + ½	1.12	200
-½ + ¼	0.79	100
-¼ + ⅛	0.56	100

Important. The quantity of sample (representative of bulk) required for this test is to be sufficient to supply the requisite minimum number of pieces per grade-size as shown in the above table, for any fraction constituting more than 15% of original sample quantity. Every sieve fraction containing more than 2% of original sample quantity, must be tested.

Alternative to using the standard gauge, if this is not immediately available, a calliper gauge may be employed. One in common use measures up to 14 cm. or 5½ in., with metric and English scales and two verniers.

The jaws of the callipers are set at appropriate distance apart for elongated pieces of the size being tested. The amount of pieces *greater in length* than distance between the jaws as set, represents elongated constituents; the elongation index is therefore calculated on the ratio of weight² of those constituents to the weight of the original sample taken for test.

FLAKINESS INDEX

This is defined as 'the total weight of the material passing the various gauges or sieves, expressed as a percentage of the total weight of the sample tested'³. Here again a special type of thickness gauge is prescribed and direct measurements are facilitated thereby⁴, or appropriate sieves having elongated slots may be used.

The sample is weighed and sieve analysis carried out; procedure is then governed by the following data⁵:

¹ *Ibid.*, Table 9, p. 30.

² Accuracy of at least 0.1% of weight of original test sample.

³ B.S. 812 : 1951, clause g, p. 30. (Revised 1960).

⁴ *Ibid.*, Fig. 7, p. 28.

⁵ *Ibid.*, Table 9, p. 30.

Size of aggregate (B.S. sieves)	Thickness gauge	Minimum no. of pieces to be tested
in.	in.	
-2 + 1½	1.050	300
-1½ + 1	0.750	300
-1 + ¾	0.525	200
-¾ + ½	0.375	200
-½ + ⅜	0.263	100
-⅜ + ¼	0.188	100

Important. The quantity of sample (representative of bulk) required for this test is to be sufficient to supply the requisite minimum number of pieces per grade-size as shown in the above table, for any fraction constituting more than 15% of original sample quantity. Each sieve fraction containing more than 2% of original sample quantity must be tested.

Alternatively, as in the case of determination of elongation index, a calliper gauge may be used with jaws set at appropriate distance apart (as in above table) for size of aggregate under test. The amount of material *passing through* the jaws as set, represents flaky constituents; flakiness index is therefore calculated on ratio of weight¹ of those pieces passing through the gauge to weight of original sample taken for test.

FREQUENCY FACTOR

The term was originally applied to the relative proportions of specific minerals or varieties of those minerals occurring in a given heavy mineral residue. It can be extended to any combination of minerals whether incoherent or in thin section of consolidated rock. There exist various methods of expressing such frequencies, in the past chiefly qualitative and visual. The only satisfactory quantitative method is that of some form of counting mineral grains² in slides under the microscope. Accuracy in assessing relative frequency of mineral occurrences depends as much on completeness of extraction of total heavy mineral residue from the sample as on actual counting, although it may not be necessary to utilize the whole residue for the count, a system of 'proportioning', as with alluvial concentrates, being adopted. Similarly, in thin section work, the slide must be as truly representative of average rock under

¹ Accuracy of at least 0.1% of weight of original test sample.

² W. F. Fleet, *Geol. Mag.*, 63, 1926, p. 505; *Proc. Geol. Assoc.*, 38, 1927, p. 1 (cf. Vol. II, Ch. IV of this book for application of frequency values to correlation by petrographic methods). See also under Micrometric Analysis, p. 273.

observation as possible, in order that the frequency factor as determined, may bear some real resemblance to actual fact. Results in any event are expressed as percentages.

GRAIN SIZE

See under Particle Size Determination, Chapter IV, p. 191; also Chapter VI, Microscopical Measurement, p. 220.

GRAVEL CONSTITUENTS

See under Petrological Examination for Nature of Components, p. 278.

HARDNESS

This is a highly variable function in minerals, but of definite diagnostic value where it can be determined with a reasonable degree of certainty. Obviously where a mineral concentrate is composed of finely divided particles, tests in accordance with the conventional Moh's Scale of Hardness (See Vol. II, Appendix III) are impracticable. With minerals around 2 mm. grain size, however, it is sometimes possible to estimate hardness, using the standard set of minerals but observing 'scratching' reactions under a microscope. Larger-size particles should offer no difficulty.

In making hardness tests in accordance with Moh's Scale, essence of success is to employ a first-class set of the standard minerals involved. Each specimen should be carefully selected as a pure true-to-type mineral; each should be well crystallized, as euhedral as possible; each should be of reasonable size to make for easy handling. Standard minerals and corresponding hardnesses according to Moh's Scale are as follows:

<i>Standard Mineral</i>	<i>Hardness (Moh)</i>
Talc	1
Rock-Salt or Gypsum	2
Calcite	3
Fluorite	4
Apatite	5
Orthoclase	6
Quartz	7
Topaz	8
Corundum	9
Diamond	10

In making the hardness test, a fresh, unweathered surface of the mineral under test should be chosen. An initial sorting test may be made if desired with the finger nail (up to 2½), glass fragment (5), a penknife (up to 6½), or flint (7). Procedure is to endeavour to scratch

the standard mineral with the test mineral, not *vice versa*. If the test mineral scratches one mineral, but not the next higher in the Moh sequence, then hardness of the test mineral lies between the two (it may actually be nearer the lower or higher value).

It is important to realize that Moh's Scale is quite arbitrary and the numbers do not represent any regular mathematical ratio as between one and another.

Precautions to be taken: (a) make sure the scratch produced on the softer mineral is new and permanent; (b) remove any dust formed and confirm scratch with hand-lens or microscope; (c) ignore any white marking which may appear when a softer mineral is used to scratch a harder one: it is probably quite superficial.

HEAVY MINERAL CONTENT

This is expressed as a percentage in terms of original sample:

$$100x/w$$

where x = weight of heavy mineral obtained after separation and w = weight of sample originally taken. The percentage is calculated on the natural rock and not on the acid-cleaned material. In some cases where bromoform of low gravity (2.75) is purposely used to segregate quartz from associated minerals, the percentage of heavy residue > 2.9 (bromoform) calculated on the total residue > 2.75 is used as a factor in correlation. The same formula applies, but in this case x = net amount of residue > 2.9 and w = amount of residue > 2.75 . Known as the 'per cent. H.R. to total H.R. factor', it is an unnecessary refinement if standard bromoform is always employed.

MICROMETRIC ANALYSIS

The mode of a rock, as it is usually interpreted, is an accurate assessment of percentages of individual minerals which make up its composition. There are several methods of approach to this problem, *e.g.* micrometric, planimetric (p. 281) and point counter systems (p. 281).

In micrometric analysis the Delesse-Rosiwal method has been traditional for over fifty years and is still a popular technique in many petrological laboratories. This involves use of linear or co-ordinating patterns of micrometer for estimating volume percentages of minerals present in a given rock sample. Linear measurements are made in several traverses of thin sections or detrital mounts under a polarizing microscope; those measurements are directly proportional to volume percentages.

Procedure is to make a number of parallel traverses by either moving the slide methodically or, better still, by means of a stage micrometer.

The total length measured should be from at least 100–200 times average diameter of the mineral grains under examination to ensure a reasonable degree of accuracy. The sum of the intercepts recorded for each mineral is reduced to a percentage of the sum of individual totals, thus an approximate volume percentage for each mineral is established¹. Using S. J. Shand's recording micrometer² (a specially designed stage pattern), much tedious work involved in the direct measurements can be obviated.

MOISTURE CONTENT (HYGROSCOPIC) OF SEDIMENTS

Hygroscopic or absorbed moisture can vary to a small extent with atmospheric humidity prevailing at time and place of determination. In the case of crushed rock or incoherent sediment, it can also be influenced by fineness of the sample. Two methods are in general use, of which the first is favoured by the author.

The procedure is to place 2 g. of the rock powder in a squat weighing bottle and dry in an oven at 110°C for 3 hours. The loss in weight is recorded as hygroscopic moisture or water.

The second method, advocated by A. W. Groves³, is to take a thin, weighed watch-glass (10–20 g.) which will comfortably fit the balance-pan, and put on to it 2 g. of powdered sample, then re-weigh. The watch-glass is placed in an oven and heated at 110°C for at least 2 hours. After heating, transfer to a desiccator, cool and weigh. The loss in weight is the hygroscopic water content.

MOISTURE CONTENT (HYGROSCOPIC) OF ASPHALT AND BITUMINOUS IMPREGNATED ROCKS

It is sometimes necessary to determine the moisture content of native asphalts, natural rock asphalts, oil-impregnated rocks, etc., and for this purpose the Dean and Stark method⁴ is normally employed. The apparatus (Fig. 36) consists of a cylindrical copper still with a flanged top to which the head is attached by means of a clamp, a heavy paper gasket between the two ensuring a satisfactory joint. A condenser and graduated receiver are fitted to the head of the still by cork or other suitable means. A ring burner is employed for heating and of dimensions which permit of its being moved up and down the still; where there is any likelihood of foaming taking place, heating is commenced from the top of the still.

¹ A. Holmes, *Petrographic Methods and Calculations*, (Murby, London), 1921, p. 312.

² *Journ. Geol.*, 24, 1916, p. 394; also A. Holmes, *op. cit.*, p. 319.

³ *Silicate Analysis*, 2nd ed., (George Allen and Unwin, London), 1951.

⁴ *Standard Methods for Testing Petroleum and its Products*, 17th ed., (Inst. Pet., London), 1958, I.P. 74/57.

A representative sample of the rock to be tested and weighing 100 g., is introduced in the still and 100 ml. of a special diluent (carrier liquid) added. The latter is petroleum spirit¹ free from water, which distils completely between 90° and 160°C., with maximum recovery of 20% at 100°C. The lid is then clamped in position and heat applied to the still, distillation being continued until no further water collects in the receiver. The volume of water is observed and its percentage by weight in the original sample calculated to nearest 0.1%.

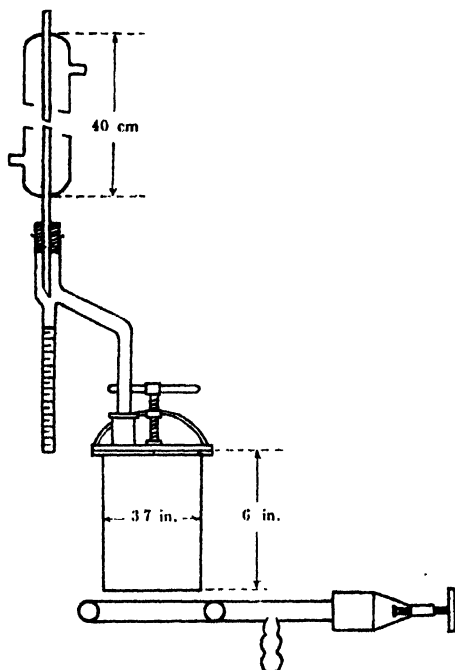


FIG. 36. Determination of Moisture Content.
(After B.S. 598: 1936, p. 24).

ORGANIC IMPURITIES

It is frequently required to ascertain the amount of organic impurities present in sands, especially if destined for use as fine aggregate in Portland cement concrete. The following is a standard method², but it must be regarded as approximate.

¹ See I.P. *Standard Methods*, 123/58.

² B.S. 812 : 1951, clause 22, p. 41. This also contains a colour chart for comparisons. (Revised 1960).

Take a 12 oz. graduated, clear-glass medicine bottle and with a wax pencil mark the $4\frac{1}{2}$ oz. line on the outside. Fill the bottle to the $4\frac{1}{2}$ oz. line with the sample of sand to be tested and add to it a 3% solution of sodium hydroxide in water to make up to 7 fluid oz. Stopper the bottle, shake vigorously, then allow to stand for 24 hours. The amount of organic impurity is assessed in terms of a standard solution or correct coloured glass¹. If the standard solution is used, this is made up by adding 2.5 ml. 2% solution of tannic acid in 10% alcohol to 97.5 ml. of a 3% solution of sodium hydroxide. This is put into a 12 oz. bottle, stoppered, shaken vigorously and allowed to stand for 23 hours. It is then shaken again and allowed to stand 1 hour before use as a comparison with the colour of the liquid above the sand. 'Solutions darker in colour than the reference standard colour have a "colour value" higher than 500 ppm. in terms of tannic acid².'

PERMEABILITY

The permeability of a porous substance is the volume of fluid of unit viscosity which passes through unit cross-sectional area in unit time under a unit pressure gradient. There is no direct connexion between porosity and permeability, although it is true that highly porous rocks are usually very permeable. This is, however, only because the pores are interconnected and it is obviously theoretically possible for a rock to have a large number of closed pores without being permeable. The porosity of a number of spheres of equal diameter is independent of their size, but their permeability depends on the size of the interstitial openings.

Under certain special conditions, the approximate value of permeability may be calculated from sieve analyses and porosity determinations, but in most cases it is preferable to make a direct determination. Full details of a method employed for oil-well samples will be found in a paper by R. D. Wychoff, H. G. Botset, M. Muskat and R. D. Reed³. This consists essentially in forcing a liquid or gas through a sample of known dimensions sealed in a brass tube and measuring the rate of flow of the fluid and the pressure gradient. Where a liquid is employed, permeability is given by:

$$K = \frac{\mu QL}{A(P_1 - P_2)}$$

where K = permeability,

μ = viscosity of liquid,

A = cross-sectional area of the core,

¹ Obtainable from Pilkington Bros. Ltd., St. Helens, Lancashire, as 'Pilkingtons $\frac{1}{8}$ in. Deep Amber Polished Plate, B.S.'

² A.S.T.M., Standards, 1952, C40-48, p. 942 (method of test the same as in B.S. 812 : 1951).

³ *Bull. Amer. Assoc. of Petrol. Geol.*, 18, 1934, p. 161.

- L = length of core,
 $P_1 - P_2$ = difference of pressure at in-put and out-put ends,
 Q = volume of liquid passing in unit time.

With a gas, rate of flow is proportional to the difference in the squares of the pressure at the in-put and out-put ends, but the formula for permeability reduces to one identical with that for liquids, except that Q now refers to the flow corresponding to the algebraic mean pressure in the flow channel.

The sample used for permeability measurements is a core, about 5 cm. in diameter and 1 cm. in length, which is cut from the rock (either parallel or transverse to the bedding plane) with a slotted brass tube fed with carborundum. The ends of the cores are 'trued' and precautions taken during this operation to avoid 'clogging' the surface pores. The core is then dried and the oil if present removed by extraction in a Soxhlet apparatus, after which it is sealed in a brass tube with hot pitch or sealing wax.

When liquids are used for permeability measurements, the core is mounted vertically with the inlet end facing downwards, so that the top surface is always kept covered with liquid and capillary forces thereby eliminated. The danger of trapping air in the pores is avoided by admitting the liquid under vacuo. Precautions are necessary to avoid 'plugging' the pores of the core through the use of water containing dissolved silicic acid or oil containing gummy substances. Such devices as filtering water through an alundum filter or storing oil in nitrogen after removing unsaturated bodies, are quite satisfactory. A further difficulty is sometimes encountered if the matrix cementing the grains together dissolves in the liquid used for making the permeability measurement, in which case the pores become 'stopped' by the detached grains. For such samples, organic liquids such as carbon tetrachloride are most convenient. With liquids at constant temperature, the rate of flow plotted against the pressure difference should give a straight line.

In addition to the precautions noted above, the core must be very carefully dried, preferably in a vacuum, to eliminate all traces of moisture when gases are employed for permeability measurements. To preserve this condition throughout the test, the gas employed must also be dried. While it is sufficient with liquids to measure differences of pressures, for gases, both the in-put and out-put pressure must be determined, as the rate of flow is proportional to the difference in the squares of these pressures. The rate of flow of the gas is measured by a water displacement method or by a meter if a high rate of flow is employed. Observations are made at several pressures and rate of flow at mean pressure plotted against difference in absolute pressures, when the result should be a straight line. Values for permeability obtained by gas measurements are in agreement with those obtained using liquids, but advantages of using gases are that (a) danger of 'clogging' pores or disintegration of sample is altogether eliminated;

(b) errors due to entrapped air are avoided; (c) assuming air is employed, there is no necessity for evacuation and (d) use of excessive pressures is avoided.

Further discussion on measurement of permeability will be found in a paper by H. J. Fraser¹, who describes porosity and permeability experiments with collections of individual spheres, also effect of particle size, shape, degree of compaction and various other factors on permeability of sediments.

Permeability as applied to determination of specific surface (see p. 130) of fine rock powder, cement, etc., is standardized procedure and from a practical standpoint may have other applications in petrographic work. The principle of the method (developed specifically for cement) consists in drawing a known quantity of air through a specially prepared bed of the substance under investigation. 'The number and size of the pores in a prepared bed of definite porosity is a function of the size of the particles and determines the rate of air flow through the bed².' In the A.S.T.M. method, the Blaine Air Permeability Apparatus is involved and is described in the standard quoted below². A similar procedure is laid down for Portland Cement in this country³. Further information on permeability (and absorption) as concerned with concrete, mortar, etc., has recently been provided by F. M. Lea⁴, also by the Road Research Laboratory (D.S.I.R.)⁵.

PETROLOGICAL EXAMINATION FOR NATURE OF COMPONENTS

With consolidated sedimentary rocks, thin section technique as described fully elsewhere in this book (Vol. II, Ch. II) is the normal method of approach. With incoherent sediments, the methods available for petrological identification of components necessarily vary according to the size-ranges represented in the sample under examination. A case in point is the frequently required quantitative estimation and identification of rock-types present in coarse and fine aggregates (gravel and sand) destined for use in concrete structures. American civil engineers demand far more detailed petrological analyses per grade size of aggregates for this purpose than is customary in this country⁶, where group classifi-

¹ Experimental Study of the Porosity and Permeability of Clastic Sediments, *Journ. Geol.*, 43, 1935, p. 910.

² A.S.T.M. Standards, 1952, Part 3, C204-51, p. 129.

³ B.S. 12: 1958, Portland Cement, Appendix A, p. 11 and Figs. 1 and 2.

⁴ *Chemistry of Cement and Concrete*, 2nd ed., (Arnold, London), 1956, p. 347.

⁵ *Concrete Roads*, (H.M. Stationery Office, London), 1955.

⁶ *Petrographic Examination of Aggregates for Concrete*, A.S.T.M., C295-52T, 1952, Part 3, p. 978.

cation of rocks, particle shape and surface texture are the normal functions determined¹.

The American procedure, which has on occasions been followed out in the author's laboratories, is most detailed, laborious and time-consuming, as will be immediately apparent from the A.S.T.M. specification cited. But the underlying principles can be and often are followed on a smaller scale in this country, with aggregates intended for concrete, coated macadam, building and other constructional purposes. This modified technique is the recommended pattern of procedure as applied to gravel, sand, crushed mixed rock aggregates etc., and is best illustrated by an example based on a typical case of this intensive kind of analysis².

The bulk sample as received is weighed. If wet, it is dried before weighing. Generally, if the weight exceeds 1 cwt., judicious quartering is necessary to reduce the bulk to manageable proportions. Supposing the material is observed to range from 2½ in. pebbles down to fine sand; procedure is then to split up the quantity taken for test into four primary gradings by sieving; these, conveniently, may be 1 in. and above, ¾ in.-1 in., ¼ in.-¾ in. and minus ¼ in. B.S. sieves. Having segregated the four fractions, further sieving of each on a series of B.S. sieves appropriate to primary gradings, is carried out. Results of sieve analyses are expressed as percentages in the usual way. Thus a quantitative estimation is obtained of the grade-size distribution of components of the bulk sample.

Sieve analyses completed, the four primary gradings are each reconstituted by re-mixing and these four main fractions form the basis of the petrographic work.

The 1 in. and plus fraction is first examined and all obviously 'like' components segregated by hand. The experienced petrologist will soon make a separation of readily identifiable rock-types in this pebble grade, e.g. limestone, vein-quartz, quartzite, sandstone, basalt, etc. Even segregation by relatively untrained personnel into colour-types, texture-types and limestone (tested with acid) helps the process enormously. Eventually a miscellaneous ill-diagnosed 'heap' emerges and with this fraction, the petrologist must perforce deal, either with hand-lens or thin sections from broken pebbles. This last procedure necessarily prolongs the investigation and should be reduced to minimum requirements for all practical purposes. Any unidentified residue, usually of badly weathered material, is labelled 'remainder'. Breaking pebbles on a steel plate with a heavy geological hammer materially aids identification of difficult components and so saves thin section preparations.

Ultimately the classification is reasonably complete and each group of 'like' components is weighed separately, results being expressed under the following headings: *Rock-Type, Per Cent. by Weight, Petrographic Description, Physical Quality, Reactivity*³.

¹ B.S. 812 : 1951, clauses 8 and 9. (Revised 1960).

² Geochemical Laboratories, ref.T.12863, 1955.

³ See p. 280.

Rock-Type. This is in accordance with standard petrographic nomenclature¹.

Per cent. by Weight. Actual quantity of each rock type present.

Petrographic Description. Colour, shape, texture, crystalline, stratified, etc.

Physical Quality. Hard to break, therefore mechanically sound and satisfactory on this score. Moderately hard, therefore fair quality. Soft, therefore poor quality.

Reactivity. Rock types determined petrologically and suspect of potential reactivity with alkalis released during hydration of Portland cement, e.g. some forms of chalcedonic silica; acid, particularly glassy, volcanic types; certain decadent dolerites² containing the mineral 'chlorophaeite' (a chloritic product of known potentiality).

Having thus dealt with the coarsest fraction and knowing the rock-types represented in that one, the next smaller size-fraction, $\frac{1}{2}$ in.-1 in., is treated in the same way, with advantage of a foreknowledge of what to expect. Similarly with the $\frac{1}{4}$ in.- $\frac{1}{2}$ in. material, which on account of size, does sometimes make precise 'spot' diagnosis more difficult and cause a build-up in thin section work. With minus $\frac{1}{4}$ in. material, the procedure is followed as far as practicable, aided by a series of microscope slides of fractions specially sieved from this primary grading, e.g. retained on 16, 30, 50, 100 and passing 100 B.S. sieves, and the use of a co-ordinate micrometer for estimating relative quantities of particles of similar composition. It is in this last phase of the analysis that experience counts, especially in diagnosis of rock-particles as distinct from associated individual mineral grains such as quartz.

In natural gravel deposits, the pebble constituents often do provide a clue to identification of the finer material, particularly where provenance is the same for both and to this extent assessment of the 'sand' fraction may be facilitated.

The final operation is amalgamation of results of the petrographical analyses of each of the four primary grade-sizes taken and calculations made in terms of the weight of bulk sample actually taken for test. The results are then recorded (in round figures) as percentages of components found in order of decreasing importance. For most practical purposes, it is unnecessary to name in the summary those components which have less than 4% occurrence, as the actual example on page 281 will illustrate.

The following analysis is that of a remarkably mixed rock gravel aggregate comprising as it does igneous, sedimentary and metamorphic rock-types. It is quoted designedly as a complicated example of this technique. Many aggregates are much simpler to deal with, in that perhaps not more than one major and a few quite minor constituents enter into their make-up.

¹ B.S. 812 : 1951, clause 9a, b, and Part 7. (Revised 1960).

² F. M. Lea, *The Chemistry of Cement and Concrete*, 2nd ed., (Arnold, London), 1956, p. 498.

<i>Rock-Types Found</i>	<i>Composition of Sample (as recorded)</i>	<i>Per cent.</i>
Andesite	Limestone	31
Basalt	Vein Quartz	18
Chert	Quartzite	11
Diorite	Serpentine	7
Gabbro	Chert	6
Granite	Basalt	6
Limestone	Sandstone	5
Quartzite	Diorite	4
Rhyolite	Remainder*	12
Sandstone		
Schist		
Serpentine		
Siltstone		100
Vein Quartz		

* Represents six out of a total of fourteen rock-types occurring in the sample of gravel analysed.

PLANIMETRIC ANALYSIS

This is in fact another version of micrometric analysis (p. 273) and makes use of the same Rosiwal principle, but employs an integrating stage fitted to the polarising microscope. In the Leitz pattern 'the integrating stage has six independent measuring spindles, by means of which the proportional amounts of six different constituents may be summed in one operation in a surface of 18mm. × 18mm. and planimetrically evaluated'¹.

Planimetric analysis is being increasingly extended in various industrial fields. Apart from obvious petrological and mineralogical quantitative determinations, mineral ores and coals are now studied by this means for their essential components. In the cement industry, the technique has been used to determine relative proportions of di- and tri-calcium silicates and matrix. In research on refractories and ceramics, estimates of inverted forms of quartz, *e.g.* tridymite and cristobalite can be accurately made; the degree of mullite conversion in certain porcelain bodies (*e.g.* sparking plugs) is an important determination by this means.

Full details of how to carry out a planimetric analysis of an object composed of various constituents, together with an actual example fully worked out, using the integrating stage, are given by the makers¹.

POINT COUNTER

The application of point counter analysis in petrological and mineralogical work, as in many other scientific fields, is one that

¹ E. Leitz, *Integrating Stage*, (Wetzlar and London), 1955.

has increased in popularity in recent years, largely due to the greater speed with which evaluations can be made (especially if automatic equipment is used) compared with planimetric methods. The principle involved in point counting consists essentially of 'sampling' the specimen at a number of *loci*. Accuracy of such analysis bears a direct mathematical relationship to the number of points actually sampled; consequently from a practical standpoint, the greater the number of points, the more accurate the results.

In the Swift Automatic Point Counter¹, a servo-operated traversing carriage is attached to the stage of a polarizing or other type of microscope and coupled to an electrical recording or counting unit under direct control of the operator. The thin section or other type of mount is positioned on the carriage in such a way that the portion or area to be analysed is embraced by traverse of that carriage. 'Depression of any push-button in the recorder unit will . . . trigger the electrical release mechanism and permit the carriage to move one step. After each identification the stage is stepped an equal distance until the carriage has reached the edge of the specimen or any agreed limit. The carriage is now restored to its starting position . . . and the next traverse selected by the vertical spacing . . . and the counting process repeated¹.'

Procedure is that the operator first identifies a mineral grain under the cross-wires of the microscope; then the appropriate push-button is pressed and the slide automatically moves lengthwise one space on to reveal the next particle for identification; the process goes on until one horizontal traverse is completed. The slide is then moved up until the next traverse position is set, counting repeated and the process continued until the whole area of mineral grains to be analysed has been covered.

The Point Counter can be used with any objectives and magnifications, including oil immersion systems, also with both transmitted and incident light.

F. Chayes used a method of intercept distances for making thin-section analysis, by modifying the activating screw on a mechanical stage. For this screw he substituted a 'notched click wheel', a click being heard when the stage had moved a given distance. A mechanical counter was employed to measure the number of clicks, which represented individual minerals identified as the thin section was traversed².

POROSITY

The porosity of a rock is the volume of the pores or air spaces it contains expressed as a percentage of the total volume of the sample.

¹ J. Swift, *Automatic Point Counter*, London, 1955.

² A simple Point Counter for Thin Section Analysis, *Amer. Min.*, 34, 1949, p.1.

$$\text{Porosity} = \frac{\text{Volume of pores} \times 100}{\text{Volume of rock substance} + \text{volume of pores}}$$

Methods by which porosities are determined fall into three main classes:

- (i) Direct methods for more or less compact rocks.
- (ii) Indirect methods for more or less compact rocks.
- (iii) Methods for loose sediments, sands, grits, etc.

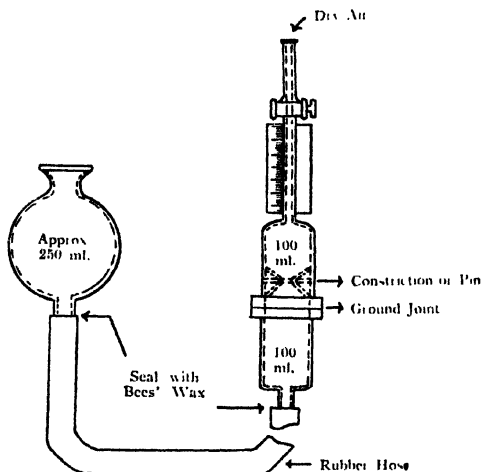


FIG. 37. McLeod Porosimeter.
(After A.S.T.M. Standards, 1933. Part II Non-Metallic Materials, p. 1084.)

(i) **Direct Methods for Compact Rocks.** The volume of open pores in a rock may be determined directly by a porosimeter, similar to that shown in Fig. 37, apparatus originally prescribed by A.S.T.M. for testing electrical porcelain¹. This consists of a cylindrical receptacle for the sample, having the top edge ground flat and connected at the bottom with a mercury reservoir. A cap fits over the top and attached to it is a capillary tube and scale for measuring the volume of air withdrawn from the sample. A constriction in the cap prevents the specimen from rising. For rocks with up to 1% porosity, the effective volume of the capillary should be approximately 0.5 ml. More porous rocks require a longer or wider capillary. The edge of the specimen should be freshly fractured and two or more pieces with a total volume about 50 ml. placed in the receptacle. The ground

¹ A.S.T.M. D116-30.

glass joint and stopcock are then greased and made airtight. Moisture is removed from the inside of the apparatus and from the specimen by completely filling the interior with mercury, closing the stopcock and then lowering the reservoir so as to create a vacuum. This is maintained for 1 minute and the reservoir then raised and the gas collected in the capillary tube expelled. The levelling bulb is now lowered and the specimen exposed to air for 1 minute, after which the level of the mercury is again raised above the stopcock and the latter turned. The reservoir is now re-lowered, a vacuum maintained for at least 1 minute and the volume of expelled air measured by raising the reservoir until the levels of the mercury in the reservoir and capillary are the same. With this particular type of porosimeter the total volume of the sample must be determined by some other means, such as weighing in water (p. 287).

(ii) Indirect Methods for Compact Rocks. The commonest method of determining porosity is by calculation from the true specific gravity of the rock substance (*i.e.* the powdered rock) and the specific gravity of the rock in bulk. The latter is here called *apparent specific gravity*, but it should be noted that the term has other meanings as, for example, a specific gravity to which the correction reducing the weights to a vacuum has not been applied.

The relationship between the porosity and the specific gravity of the rock in bulk and powder form is as follows:

Let P_1 = Porosity of the rock,

G_1 = True specific gravity (C.G.S. units),

G_2 = Apparent specific gravity of the rock in bulk (C.G.S. units),

d = density of water at the temperature of test,

then 1 ml. of rock in bulk weighs $G_2 d$.

But this contains $1 - P_1/100$ ml. of rock substance,
which will weigh:

$$dG_1 \left(1 - \frac{P_1}{100} \right)$$

$$\text{whence } G_2 = G_1 \left(1 - \frac{P_1}{100} \right)$$

$$\text{or } P_1 = \frac{100 (G_1 - G_2)}{G_1}$$

The apparent specific gravity is usually determined on pieces of rock about 2 in.-3 in. in diameter which, for precise work, should be reserved and later dried and crushed to a powder for the determination of true specific gravity. It is essential that the sample is large enough to be representative; the larger the pores in the rock, the bigger must be the sample. The piece of rock is first dried to constant weight at 100°C., a process which may take as long as 3 days. It is then weighed and placed in a vacuum desiccator of the type shown in Fig. 38. The pressure is reduced to 1 mm. and distilled water, which has previously been

boiled and cooled, admitted through the tap-funnel until the specimen is completely covered. The latter is left overnight and in the morning is suspended by a thin wire in water and weighed, a correction being applied for the weight of the wire in water. It is then removed and surface dried by wiping with a cloth and rapidly weighed.

If W_1 = Weight of dried piece of rock,
 W_2 = Weight of rock in water,
 W_3 = Weight of surface-dried rock,
 G_3 = Apparent specific gravity,

then
$$G_3 = \frac{W_1}{W_3 - W_2}$$

This method is not recommended where large pores are present, *e.g.* coke, and in such cases it is advisable to use a wax coating method (*infra*).

In the absence of closed pores, the specific gravity (G_3), calculated from the formula

$$G_3 = \frac{W_1}{W_1 - W_2}$$

should be the same as the specific gravity of the powdered rock (G_1). If closed pores are present, the specific gravity of the powdered rock will be the higher of the two and the percentage of closed pores (P_2) will be given by

$$P_2 = \frac{100 (G_1 - G_3)}{G_1}$$

A vacuum desiccator is not essential in porosity measurements, but it enables a determination of closed pores to be made. If only the apparent specific gravity of the rock is required, it is sufficient to place a piece in water for 24 hours and then weigh it in water and surface-dry it. The apparent specific gravity may then be calculated from the formula given on p. 284. Before crushing to a powder to ascertain the true specific gravity, the rock must again be dried to constant weight.

An alternative method of determining apparent specific gravity is to apply a wax coating to the dried and weighed sample. In this case a layer of molten wax about $\frac{1}{16}$ in. thick is brushed over the surface of the rock, which is then re-weighed, suspended in water and again weighed.

If W_1 = Weight of dry rock,
 W_2 = Weight of dry rock + wax,
 W_3 = Weight of dry rock + wax in water,
 S = Specific gravity of wax,

then volume of wax =
$$\frac{W_2 - W_1}{S}$$

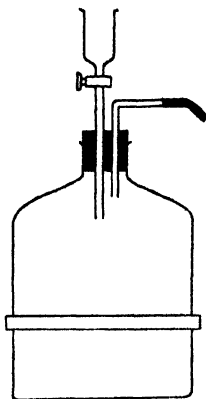


FIG. 38. Vacuum Desiccator.

$$\text{and specific gravity of rock} = \frac{W_1}{W_1 - W_2 - [(W_2 - W_1)/S]}$$

For the true specific gravity determination, the rock is dried to constant weight and crushed to such a state of division that pores are eliminated. For most purposes a powder completely passing a 100 B.S. sieve is suitable. A clean, dried and weighed specific gravity bottle is two-thirds filled with the powder and re-weighed, after which it is placed in a vacuum desiccator carrying a tap-funnel, as shown in Fig. 38. The desiccator is evacuated to 1 mm. pressure and distilled water, which has previously been boiled and cooled, added slowly through the tap-funnel until the bottle is full, when the pressure is slowly increased to atmospheric. If the level of the water in the neck of the bottle is carefully watched during the latter process, it is easy to see whether any air bubbles are present, as they will cause the level to fall when air is admitted to the desiccator. If bubbles are absent, the bottle is removed, placed in a bath of water at 15.5°C. and allowed to remain there for 30 minutes, at the end of which time the stopper is inserted and the bottle wiped and re-weighed.

If W_1 = Weight of bottle full of distilled water at 15.5°C.,

w = Weight of bottle,

W_2 = Weight of bottle + rock,

W_3 = Weight of bottle + rock + water to fill bottle at 15.5°C.,

then

$$G_{15.5}^{\text{liq}} \text{ of rock} = G_1 = \frac{W_1 - w}{(W_1 - w) - (W_3 - W_2)}$$

Where a suitable vacuum pump is not available, wetting will, in general, be more easily achieved with an organic liquid such as kerosene, toluene or carbon tetrachloride than with water. The greater volatility and coefficient of expansion of organic liquids necessitate more care in carrying out the determination, especially in hot weather, but losses due to evaporation may be minimised if after immersing the bottle for 30 minutes in a water bath at 15.5°C. the stopper is inserted and quickly wiped and the bottle transferred to a bath of very cold water until a bubble of air forms in the neck of bottle. This gives ample time to complete drying and weighing the bottle before the solvent emerges from the stopper. Where a liquid other than water is employed, the specific gravity of the rock is given by

$$G_1 = \frac{(W_1 - w) \times G_4}{(W_1 - w) - (W_3 - W_2)}$$

where G_1 = specific gravity of liquid at 15.5°C. compared with water at the same temperature and the remaining symbols have the same meaning as before.

A convenient procedure where the determination is to be carried out at normal pressure is to weigh the specific gravity bottle and fill it to about quarter of its capacity with the liquid to be employed. The

powdered rock is weighed out on a watch glass and transferred with a camel-hair brush to the bottle by a small glass or metal funnel with a very short stem. More liquid is added when the powder rises above the surface. After all the powder has been added, the bottle is nearly filled with liquid and well shaken, after which the determination is completed in the normal manner. By adding the rock powder to the liquid instead of *vice versa* it will be easier to eliminate air bubbles.

(iii) Methods for Loose Sediments etc. In general the methods adopted for loose sediments consist in filling a suitable container of known volume by some standard procedure which enables the same degree of compaction to be easily reproduced and then either calculating pore space from the specific gravity of the material or measuring the quantity of water required to fill the interstices between the grains.

The apparatus commonly used for the latter purpose consists of a hollow metal cone of capacity $\frac{1}{10}$ cu. ft., which is connected at the base with a measuring cylinder by means of a piece of rubber tubing and a clip. The measuring cylinder is filled with water to the top mark and the clip opened. Water is allowed to enter the cone until it appears above the level of the sand and the volume so admitted, expressed as a percentage of the volume of the cone, gives the porosity or void content of the sediment.

The results obtained by such methods are not always trustworthy, as not only is it difficult to devise a method of filling which will always give a reproducible degree of compaction, but also the interstices of the sand grains are usually not completely filled with water unless the latter is admitted under a vacuum. It is preferable, therefore, to determine the void or porosity content of sediments by calculation from the weight of a known volume compacted under carefully standardized conditions. F. H. King¹ employed for this purpose a cylindrical metal or glass container, internal diameter 5.8 cm., internal height 3.5 cm., with a circular glass lid 6.3 cm. in diameter, ground on one side. The volume of the container is first found by filling it with distilled water and sliding on the glass lid, so that no air bubbles are present, after which it is dried and weighed. The container is emptied and dried and the sample admitted in a fine stream either from a small funnel or by other suitable means. During this process the container is slightly tilted and gradually rotated and at the same time its bottom edge lightly tapped on the bench. It is slightly overfilled and the excess removed by sliding the glass plate gently across the top of the jar. The method gives the maximum degree of compaction corresponding with the minimum void content. Further tapping should not result in any diminution in volume.

If w = Weight of water to fill the container,
 W = Weight of sand to fill the container,
 s = Specific gravity of sand,

¹ U.S. Geol. Surv., 19th An. Rep., 2, 1897-8, p. 207.

then the porosity or void content (P) is given by:

$$P = \frac{w - (W/s)}{w} \times 100$$

and weight per cu. ft. (consolidated) (D) is given by:

$$D = \frac{62.4W}{w} \text{ lb.}$$

Methods suitable for mineral aggregates, sands and fillers are now standardized¹ and follow the general principle given above, in that for each type of material, procedure is to calculate porosity (or, as it is often called, void content) from volume weight of the material (p. 265) and its specific gravity (p. 292) (or density (p. 269)).

REACTIVE COMPONENTS IN GRAVEL AGGREGATES USED IN CONCRETE

In the United States and to a more limited extent in this country, potential reactivity with alkalis released during hydration of Portland cement, with certain gravel components, is a determination sometimes sought, especially if there is reason to believe that specific suspect rock-types in this connexion are present in strength and could cause abnormal expansion in concrete design when using high-alkali cement. Methods employed for this purpose are either petrographic (p. 280) or chemical. In this section chemical procedure will be briefly described. It is based on an A.S.T.M. Standard².

The basic principle of the method is the reaction of the aggregate to a solution of sodium hydroxide carried out under strictly controlled laboratory conditions. Full details of procedure are given in that Standard. Aim is to determine the amount of dissolved silica and this can be done (after the reaction procedure has been followed) either gravimetrically or photometrically. Reduction in alkalinity is also part of the determination.

In mixed-size gravel components, such as were described under the petrological heading (p. 178), it is customary to split the bulk sample into primary gradings as there detailed and carry out determination of concentration of dissolved silica and reduction of alkalinity on each grade. Results are expressed in terms of (Sc) (millimoles/litre) and (Rc) (millimoles/litre) respectively.

'A deleterious degree of alkali-reactivity is indicated if the aggregates are shown to contain proportions of reactive substances in excess of 0.25% to 5% by weight, depending upon the identity of

¹ B.S. 812 : 1951, Sampling and Testing of Mineral Aggregates, Sands and Fillers. (Revised 1960).

² A.S.T.M. Standards, 1952, C289-52T, p. 943. See also F. E. Jones, Nat. Bldg. Res. Studies, (H.M.S.O., London), 14, 15, 16, 1952 and refs. cited.

the reactive constituents; are characterized by a ratio Sc/Rc greater than 1 as a result of the chemical test; . . .¹

Alkali-Aggregate reactions are discussed in some detail by F. M. Lea² who, considering expansion and cracking of concrete due to this cause, says: 'The reaction leads to the formation of an alkali silicate gel and sets up expansive forces . . . Both a relatively high content of alkali in the cement and the presence of particular reactive constituents in the aggregate are necessary for this reaction to occur and the trouble thus arises from a combination of two incompatible materials.'

ROUNDNESS

There persists a certain cloud of confusion among some students and others regarding those physical properties of sediments concerned with roundness, shape, size and sphericity of particles in descriptive petrology, especially where no quantitative data are either demanded or implied. For this reason, these functions are treated separately here. Strictly interpreted, roundness of a particle, or pebble for that matter, means that edges and corners are rounded; this has nothing whatever to do with particle shape, size or sphericity, although these are necessarily linked in a morphological sense.

It is, indeed, relatively seldom that quantitative expression of roundness *per se* enters into petrographic essays, preference still being for those qualitative, subjective terms 'rounded', 'subangular', 'angular', etc., (incidentally essentially shape characteristics), simply because time involved in precise determination of roundness is usually out of all proportion to practical value of results, except in certain special lines of research.

None the less, quantitative data on sedimentary rocks have always been, and still are, fundamental aims in evolution of this science and wherever they can replace the perhaps more colourful but less decisive descriptive terms, their achievement is always a matter of serious aim. To this end, American petrographers, as also in recent years their colleagues in this country, have been particularly active in this field in the past, as references to original literature on this phase of the subject bear witness.

H. Wadell some years ago pioneered certain quantitative aspects of particle mensuration, including roundness, which are still sought in detailed, precision work on sedimentary rocks at the present

¹ R. C. Mielenz and L. P. Witte, *A.S.T.M.*, **48**, 1948, pp. 1087-96 and refs. cited.

² *Chemistry of Cement and Concrete*, 2nd ed., (Arnold, London), 1956, pp. 493-4, and refs. cited.

time¹. His conception of roundness is the arithmetical mean of the roundness of individual edges or corners in a two-dimensional plane divided by the number of those edges or corners.

To express this thesis in practical terms, a particle to be measured for roundness is enlarged (or reduced, *e.g.* pebble) by geometric, photographic, projection or other means to a standard size of 70 mm. Small circles are inscribed in this replica at each corner so that edges of the corner are tangential to each circle. A larger circle, maximum diameter that can be inscribed inside the replica without transgressing its boundary, is drawn. Radii of small and large circles are measured. Roundness is equivalent to the sum of roundness of individual corners divided by the number of corners in the two dimensional plane of measurement, and is given by the formula:

$$\text{Roundness} = \frac{\sum r}{N}$$

where R = radius of maximum circle,

Σ = summation,

r = radius of curvature of corner,

N = number of corners measured.

It is obvious that the above measurements do not take into account the third dimension, but for all practical purposes that is a refinement usually ignored; an assumption is made that the roundness value found by this method is for all practical purposes an adequate definition of this function of the particle measured. It will be equally obvious that if several particles containing several corners are involved, this technique is both tedious and exceptionally time-consuming.

For further information on this subject, the reader should consult the references given below².

SHAPE

The configuration or form of sedimentary rock particles is more often than not described qualitatively, such terms as rounded, spherical, irregular, subangular, angular, elongated, flaky, etc.,

¹ Volume, Shape and Roundness of Rock Particles, *Journ. Geol.*, **40**, 1932, p. 443.

Sphericity and Roundness of Rock Particles, *Journ. Geol.*, **41**, 1933, p. 310.

Volume, Shape and Roundness of Quartz Particles, *Journ. Geol.*, **43**, 1935, p. 250.

Volume, Shape and Shape Position of Rock Fragments in Openwork Gravel, *Geografiska Annaler*, 1936, p. 74.

² F. H. Pettijohn, *Sedimentary Rocks*, (Harper, New York), 1949.

E. E. Wahlstrom, *Petrographic Mineralogy*, (Wiley, New York), 1955, p. 332 and refs. cited, p. 358.

W. H. Twenhofel and S. A. Tyler, *Methods of Study of Sediments*, (McGraw-Hill, New York), 1941, Ch. IX, p. 134 and refs. cited, pp. 137, 152-3.

being used to denote this particular characteristic. But the disadvantage of using these terms is that different observers have different ideas as to exactly what they mean and some quantitative classification is obviously desirable. There have been several workers in this field.

F. G. Tickell's¹ method of determining shape depends on establishing the ratio of the area of a particle as observed in one plane to the area of the smallest circle which will circumscribe it.

T. Zingg² expresses particle shape in terms of maximum, intermediate and minimum intercepts (length, breadth, width, or length, width and thickness) and his method is to plot ratio of intermediate intercept (*b*) to maximum intercept (*a*) against ratio of minimum intercept (*c*) to intermediate intercept (*b*) from which is deduced:

Class	<i>b/a</i>	<i>c/b</i>	Shape
I	$>2/3$	$<2/3$	oblate, discs, tablets
II	$>2/3$	$\sim 2/3$	equiaxial, equant, spherical
III	$<2/3$	$<2/3$	triaxial, blades
IV	$<2/3$	$\sim 2/3$	prolates, rods, rollers.

One objection to this method is that it introduces a number of shape-terms not commonly employed in British petrography. F. G. Tickell's method is at least simple and probably as accurate a means of shape classification as any other.

Quantitative estimation of elongation (p. 269) and flakiness (p. 270) has already been discussed in this Chapter. Flatness coefficient³ can be calculated using the formula:

$$F = \frac{a + b}{2c}$$

where *F* = coefficient of flatness,
a = maximum intercept,
b = intermediate intercept,
c = minimum intercept.

C. K. Wentworth⁴ calculated the mean diameter *D* of a single pebble from the formula:

$$D = \sqrt[3]{(D'D''D''')}$$

¹ *The Examination of Fragmental Rocks*, (Stanford University Press, Ca.), 1939.

² Beitrag zur Schotteranalyse, *Schweiz. Min. u. Pet. Mitt.*, **15**, 1935, pp. 39-140.

³ E. E. Wahlstrom, *Petrographic Mineralogy*, (Wiley, New York), 1955, p. 322.

⁴ Shape of Pebbles, *U.S. Geol. Surv., Bull.* **730**, 1922, p. 91. U.S. Geol. Surv., *Prof. Paper* 131, 1923, p. 83.

A Laboratory and Field Study of Cobble Abrasion, *Journ. Geol.* **27**, 1919, p. 507.

where D' , D'' and D''' are respectively length, breadth and thickness measured. His roundness ratio is given by:

$$\frac{r_1}{R} = \frac{2r_1}{D}$$

where r_1 is radius of curvature of the sharpest edge and R is roundness or radius of maximum circle.

Flatness he derives from:

$$\frac{D' - D''}{D'''}$$

where D' , D'' , D''' are respectively the length, breadth and thickness of the particle measured, or it may be given by:

$$\frac{r_2}{R}$$

where r_2 = 'radius of curvature in the most convex direction on the flattest developed face or portion of the surface'¹. The radii are measured by a contact method with a gauge similar to that used by opticians to measure curvature of lenses, while the values of r_1/R and r_2/R for each pebble are plotted on double logarithmic chart, the former as ordinate the latter as abscissa.

A. C. Tester² proposed a method based on the ratio of the length of the original surface or edge of a particle to the portion abraded. He employs the terms rounded (81–100%), sub-rounded (61–80%), curvilinear (41–60%), subangular (21–40%) and angular (0–20%), corresponding with the percentages of abrasion actually measured by determining the length of the lines representing projected edges of the particle under examination; these percentages are quoted in parenthesis above.

SIEVE ANALYSIS

This is fully described in Chapter IV, p. 164.

SPECIFIC GRAVITY

Methods suitable for determination of specific gravity may be classified as follows:

(A) *Hydrostatic Method of Weighing in Water*. This has been described above under 'Porosity' (p. 282). The method is not generally used for incoherent sediments but is suitable for compact rocks.

(B) *Displacement Method*. This is commonly employed for incoherent sediments. A suitable flask for this determination is the Le

¹ C. K. Wentworth, *ibid*.

² The Measurement of the Shapes of Rock Particles, *Journ. Sed. Pet.*, 1, 1931, p. 3.

Chatelier type with a graduated neck (Fig. 39). The flask is filled with kerosene to one of the marks below the bulb in the neck, after which it is immersed in water at 20°C. for half an hour. Approximately 50 g. of the dried material are accurately weighed and slowly introduced into the flask, due precautions being taken to prevent the material adhering to the neck above the level of the kerosene. Air-bubbles are eliminated by gently tapping the flask on a pad. The flask is then replaced in the water bath and after half an hour the level of the liquid is observed. The difference between the two readings gives the volume of the sample and enables the density at 20°C. to be easily calculated. The density of a sediment at 20°C. differs from its specific gravity (also compared with water at 20°C.) by about three parts in a thousand, but as this is also approximately the limit of accuracy of the method, it is not usual to apply any correction when specific gravity is required.

(C) *Jolly Spring Balance Method.* This is an approximate method suitable for small specimens. First of all a reading *a* of the bead pointer is taken. The specimen is then placed in the upper pan and a new reading *b* taken. The specimen is then transferred to the lower pan in water, the height of the beaker adjusted and a third reading *c* taken. Then *b* - *a* is proportional to the weight of the specimen in air and *b* - *c* to its loss in weight in water, whence

$$\text{Specific gravity} = \frac{b - a}{b - c}$$

(D) *Specific Gravity Bottle Method, for Sands and Incoherent Sediments.* This procedure has been completely described under 'Porosity' (p. 286).

(E) *Sollas Diffusion Column (Methylene Iodide Method) for Isolated Mineral Fragments.* This is a method developed many years ago by W. J. Sollas for simultaneous determination of specific gravities of different minerals in a concentrate¹. Although not often employed nowadays, it is none the less appropriate to certain special cases. Use a test-tube and pour in about 2 ml. methylene iodide and then (carefully) 10 ml. benzol. Allow the tube to stand (corked) until diffusion

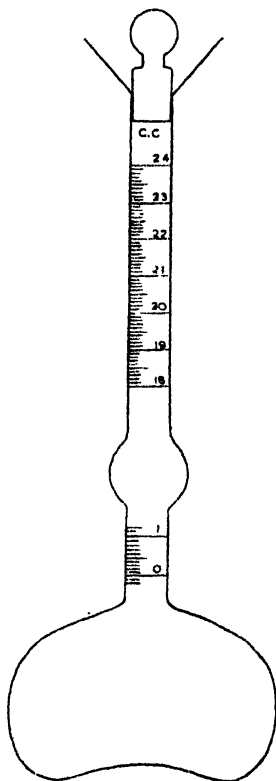


FIG. 39. Le Chatelier Flask.

¹ W. J. Sollas, *Journ. Roy. Geol. Soc. Ireland*, 7, 1886, p. 35.

has taken place, usually about 24 hours. Then insert a fragment of the mineral M , the sp.gr. of which is required and two fragments of substances A and B , the known sp.gr. of which are respectively $>$ and $< M$ (found by trial from selection of previously tested fragments). A scale should be clamped behind the tube so that the distances of M from B and A are comparable.

Then if b = sp.gr. of B , a = sp.gr. of A and m = sp.gr. of M ,

$$\frac{a - m}{m - b} = \frac{AM}{BM}$$

where AM is distance of M from A and

BM is distance of M from B .

$$\text{Whence } m = \frac{bAM + aBM}{AM + BM}$$

(F) *Other Methods.* These include the Walker Steel-Yard Balance (for large specimens) and the Westphal Balance (chiefly for liquids). These are described fully by A. Holmes¹ and H. Miers².

SPECIFIC SURFACE

This may be defined as the total surface area of finely divided mineral matter, e.g. rock-powders, fillers, cement, etc., expressed in square centimeters per gram, and its determination is, in effect, a method of measuring fineness. There are different ways of arriving at the specific surface of a sample of finely divided material and these are described in detail by F. M. Lea³. The method generally favoured today was first developed by F. M. Lea and R. W. Nurse⁴, following work by P. C. Carman⁵ on flow of liquids through powders coarser than cement. It is based fundamentally on air-permeability of a given bed of cement and employs a permeability apparatus coupled up to a manometer and flowmeter. This is the standard procedure⁶ laid down in B.S. 12 : 1958 and both apparatus and method are described therein, also in more detail, with illustrations, in F. M. Lea's book⁷.

Summarily, as applied to cement for example, the operations are as follows:

- (a) A requisite quantity of cement is weighed, to form a bed of porosity 0.475 (density of sample being known or must be predetermined).

¹ *Petrographic Methods and Calculations* (Murby, London), 1921, Chapter II.

² *Mineralogy*, 2nd ed. (Macmillan, London), 1929, p. 211.

³ *Chemistry of Cement and Concrete*, 2nd ed. (Arnold, London), 1956.

⁴ *Journ. Soc. Chem. Ind.*, **58**, 1939, p. 227.

⁵ *Journ. Soc. Chem. Ind.*, **57**, 1938, p. 225; **58**, 1939, p. 2.

⁶ *Portland Cement, Ordinary and Rapid Hardening*, (British Standards Institution).

⁷ *op. cit.*, p. 327.

- (b) The bed is compacted by plunger in the permeability cell which is then connected up with manometer and flowmeter.
- (c) Dry air is passed through the cement bed for five minutes and differences in levels in manometer and flowmeter thereafter made.
- (d) The ratio of difference in level of manometer across the cement bed to difference in level across capillary of flowmeter is calculated. The square root of this ratio is multiplied by a constant and the result is the specific surface of the cement sample in square centimetres per gram.

For the particular apparatus required in this method, the formula is as follows:

$$S = \frac{14}{\sigma(1 - \epsilon)} \sqrt{\left(\frac{\epsilon^3 A h_1}{CL h_2} \right)}$$

where C = flowmeter constant,
 L = height of cement bed,
 h_1 = manometer reading,
 h_2 = flowmeter reading,
 σ = density of cement,
 ϵ = porosity of cement,
 A = cross-sectional area of bed (sq. cm.),
 S = specific surface.

As F. M. Lea points out: 'For any one apparatus this (formula) further simplifies to:

$$S = K\sqrt{(h_1/h_2)}$$

where K is a constant varying only with the cement density¹.

In B.S. 12 : 1958, it is laid down that ordinary Portland cement shall have a minimum specific surface of not less than 2,250 sq.cm./g., and rapid-hardening Portland cement, a minimum of 3,250 sq.cm./g.

SPHERICITY

This is not the same thing as roundness (p. 289), since a particle or pebble may be well rounded and yet not approach a sphere. For practical purposes the sphericity value of a particle may be considered as the diameter of a sphere of the same volume as the particle divided by the diameter of the circumscribing sphere².

Procedure with small particles is to use a planimeter to measure the area of a projection of the largest face of the particle. The sphericity (S) of the particle is given by:

$$S = d/a$$

where d = diameter of circle of equal area to the projection,
 a = diameter of smallest circle circumscribing the projection.

¹ *op. cit.*, p. 329.

² H. Waddell, *Sphericity and Roundness of Rock Particles*, *Journ. Geol.*, 41, 1933, pp. 310-31.

In the case of larger particles, the volume is first determined by water displacement method in a graduated cylinder and then the diameter of the circumscribing sphere measured; the assumption is made that the latter is equivalent to the longest diameter of the particle.

SURFACE TEXTURE (TEXTURAL ANALYSIS)

This is essentially physical appearance of the surface of a consolidated rock or incoherent rock-particles and is determined by relative sizes, shapes, disposition, arrangement and degree of crystallinity of their constituents. Texture in the broader sense, however, may not in itself be confined merely to superficial characteristics; it may, frequently does in consolidated sedimentary rocks, vary internally within a given stratigraphical environment or it may be a uniform property of such development. In general, descriptions of surface texture are qualitative, when results of visual examination of representative particles or aggregate components are expressed in terms commonly understood.

For all practical purposes, the surface texture of aggregates, as laid down in B.S. 812 : 1960¹, is as good a guide to textural descriptions as any other and is here quoted:

GROUP	SURFACE TEXTURE	CHARACTERISTICS	EXAMPLES
1	Glassy	Conchoidal fracture.	Black flint, vitreous slag.
2	Smooth	Water-worn, or smooth due to fracture of laminated or fine grain rock.	Gravels, chert, slate, marble, some rhyolites.
3	Granular	Fracture showing more or less uniform rounded grains.	Sandstone, oolites.
4	Rough	Rough fracture or fine- or medium-grained rock containing no easily visible crystalline constituents.	Basalt, felsites, porphyries; Carboniferous limestone.
5	Crystalline	Containing easily visible crystalline constituents.	Granite; gabbro, gneiss.
6	Honeycombed and Porous	With visible pores and cavities.	Brick, pumice, foamed slag, clinker, expanded clay.

¹ Sampling and Testing of Mineral Aggregates, Sands and Fillers, Table 3.

To the above, may be added other words (with examples) denoting particular textures or irregularities, often found in the literature:

<i>dented:</i>	water-worn flint in gravels,
<i>etched:</i>	differential weathering,
<i>frosted:</i>	sparkling, coarsely crystalline limestone,
<i>furrowed:</i>	slickensided shale,
<i>grooved:</i>	similar to furrowed,
<i>ridged:</i>	warped sediments,
<i>scratched:</i>	glacial boulders,
<i>striated:</i>	glacial boulders,
<i>vesicular:</i>	vapour cavities, slag.

The quantitative approach to textural analysis directed more particularly perhaps to clastic sediments, is by means of mechanical¹ and shape determinations² previously described.

VOID CONTENT OF DRY COMPACTED FILLER

This determination requires the use of special apparatus, described and figured in B.S. 812 : 1951³, which also gives full details of how to carry out the test, made in triplicate, using a fresh sample of filler for each determination. The dry void content is given by:

$$1 - \frac{W}{A.d.S}$$

where W = weight of filler bed in g.,
 S = absolute specific gravity of filler,
 d = depth of compacted filler bed in cm.,
 A = cross-sectional area of cylinder in sq. cm.

VOIDS

See under Porosity (p. 282).

VOLUME WEIGHT (OR WEIGHT PER CUBIC FOOT)

See under Bulk Density etc., (p. 265).

WATER ABSORPTION

The water absorption of a rock is the percentage by weight of water absorbed under certain prescribed conditions. Among other factors it is influenced by the size of sample, the time of immersion and temperature of water during immersion; for this reason conditions under which the test is being carried out should always be stated. In some laboratories it is the practice to immerse the dry rock in water for 24 hours, in others for 3 days. The water may or may not be raised to the boiling point and the size of sample may vary from

¹ Chapter IV.

² p. 290.

³(Revised 1960).

about 50 g. to several kg. As a rule not more than half of the total pores in rocks used, for example, for road purposes can be filled by simple immersion, even though this be prolonged for several days. At the outset the water enters comparatively rapidly, but thereafter the rate soon diminishes.

The method formerly adopted by the British Standards Institution¹ for determining the water absorption of stone to be used in road carpets is still applicable to many other cases and is as follows:

'At least three roughly cubical samples of the stone to be tested shall be selected of approximately 50 grammes each in weight; sharp edges shall be filed down and the samples carefully brushed to remove any loose fragments.

'The samples shall then be placed in an ordinary air-oven fitted with a thermometer and maintained at a temperature of from 100°C to 110°C for at least 72 hours. The samples shall then be taken out of the oven, allowed to cool down in a desiccator and *immediately* weighed to obtain their dry weight (W)².

'The samples shall then be placed in a suitable trough and distilled water allowed to creep over them until they are completely immersed in about 4 hours, and they shall be left thus immersed for at least 72 hours to ensure maximum saturation.

'Each sample shall then be taken out of the trough, and, after first removing loose surface moisture with an absorbent cloth (a piece of smooth linen towel is very suitable), weighed *immediately* to obtain its saturated weight in air (S).

'The amount of absorption expressed as a percentage of the dry weight is then obtained from the formula:

$$\text{Absorption} = \frac{S - W}{W} \times 100$$

A slightly different procedure is generally followed where the rock is in the form of an aggregate intended for use in concrete. A representative sample weighing above 3,000 g. for aggregates containing pieces up to 1½ in. in size, is well washed and dried to constant weight. It is then immersed in water for 24 hours and at the end of this period the water is poured off and the aggregate dried by wiping with an absorbent towel and immediately weighed. In order to minimize the error due to loss by evaporation, it is advisable to have two operators to carry out the latter operation. The aggregate (surface-dry) is then placed in an oven at 100°C and again dried to constant weight. The water absorption of the aggregate is the difference between the surface-dried weight and the final weight, expressed as a percentage of the final weight.

WEIGHT PER CUBIC FOOT

See Bulk Density etc., (p. 265).

¹ B.S. 594 : 1935, Appendix E, p. 29.

² A physical balance to weigh 100 g. in each pan and sensitive to 5 milligrammes is sufficiently accurate.

CHAPTER VIII

OUTLINES OF METHODS IN CHEMICAL ANALYSIS OF SEDIMENTARY ROCKS, CALCULATIONS AND INTERPRETATIONS, WITH TYPICAL EXAMPLES¹

Introduction—Sedimentary Rock Constituents—Preparation of Rock-Samples for Analysis—Minimum Quantities available for Analysis—Methods of Analysis (General)—Methods of Analysis (Specific)—Calculations—Mineralogical Interpretation of Oxides found by Chemical Analysis—Reporting Analytical Results—Type Analyses of Sedimentary Rocks.

INTRODUCTION

ONE of the specialist departments in the author's laboratories has for many years been devoted to chemical analyses of minerals and rocks of all types. In course of time the chemists concerned have met a problem which perhaps only independent testing authorities have constantly to face, *viz.* a fine point of distinction between conventional, exhaustive, time-consuming silicate analyses, often for academic purposes, and those made to meet many and varied industrial demands. The former can involve determination of twenty or more constituents, especially if rare or trace-elements are sought additional to essential elements and oxides as normally returned. Time taken may, often does, run into weeks, especially when multiple samples are under examination or, if at the end of it all, summation within permitted tolerances, 99·75-100·5%, fails to be achieved.

Commercial-type analyses, although frequently implying similar technique to that pursued in more elaborate designs, are more easily restricted to determination of essential components and with sedimentary rocks in particular, the conventional minimum

¹ This chapter has been written by the author in conjunction with A. H. Clarke, M.Sc., F.R.I.C., Assoc. F.Inst.Pet., Chief Chemist, Geochemical Laboratories.

of thirteen constituents required by normal silicate analyses (igneous rocks), may in some cases be superfluous, *e.g.* high silica sand, pure limestone. In a majority of industrial analyses, economy in time is mandatory simply because results are urgent, either as routine control on production or because they are vital to important development schemes under way. This does not, however, in any event imply a policy of sacrificing accuracy to speed. It does mean that wherever short-cut methods are applicable, these are embraced as soon as the trend of analysis for any particular sample is decided upon.

As experience in this exacting field of inorganic chemical analysis is gained, there gradually evolves a sense of rapid *ad hoc* assessment of minimum requirements in mineral and rock analyses destined for varied economic uses, as compared with the more leisurely and perhaps fundamental investigations in geochemical research work; in the latter case it is customary for the investigator to state precisely the nature and number of individual constituents he requires determining, leaving it to the analyst to proceed beyond his terms of reference if, during the course of his examination, the presence of other constituents is suspected. This applies equally to igneous, metamorphic and sedimentary rocks. Here, however, we are only concerned with the latter group which, by the very nature of its make-up, does often permit of some simplification in approach to problems involved in chemical diagnosis.

With these ideas in mind, this chapter has been written, primarily to guide laboratory procedure when dealing with the major sedimentary rock-types described in Vol. II, Ch. II. The approach to the subject is both chemical and petrological; but it is stressed at the outset that, beyond *outlines* as restricted by title, no attempt is or could be made to more detailed treatment such as will be found in the literature¹.

In the classification of sedimentary rocks laid down in Vol. II, Ch. II, fundamental groups are as follows:

(A) MECHANICAL ORIGIN

Arenaceous: *e.g.* sandstone, quartzite.

Argillaceous: *e.g.* clay, shale.

¹ W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, *Applied Inorganic Analysis* (with Special Reference to the Analysis of Metals, Minerals and Rocks), 2nd ed., (Wiley, New York), 1953.

A. W. Groves, *Silicate Analysis*, (Allen & Unwin, London), 2nd ed., 1951.

H. S. Washington, *The Chemical Analysis of Rocks*, (New York), 1930.

A. Holmes, *Petrographic Methods and Calculations*, (Murby, London), 1923.

W. F. Hillebrand, *The Analysis of Silicate and Carbonate Rocks*, U.S.G.S., Bull. 700, 1919.

(B) ORGANIC ORIGIN

Calcareous: *e.g.* limestone, chalk.

Siliceous: *e.g.* chert, flint.

Ferruginous: *e.g.* bedded ironstone.

Carbonaceous: *e.g.* coal, oil shale, asphalt.

Phosphatic: *e.g.* phosphate deposits.

(C) CHEMICAL ORIGIN

Calcareous: *e.g.* dolomite.

Ferruginous: *e.g.* certain iron ores.

Siliceous: *e.g.* sinter.

Saline: *e.g.* chlorides, sulphates, nitrates, etc.

Now considered from a strictly chemical standpoint, these several rocks can be conveniently re-grouped as regards analytical plan.

All arenaceous varieties are susceptible to treatment as relatively high silica-bearing types and are subject to processes implied by silicate analysis as such, although usually far less complicated than those concerned with the more diversely mineralized crystalline igneous and metamorphic rocks.

The argillaceous sediments are again problems in silicate determination, sometimes relatively straightforward, often, however, presenting considerable difficulties in manipulation and certainly demanding a high degree of skill in their mineralogical interpretation.

Calcareous rocks, *i.e.* those containing relatively high percentage of carbonates, require different treatment, usually reasonably simple, although when silica or silicates are present in force, the analysis can soon develop into a silicate problem and has to be pursued accordingly.

Siliceous rocks such as chert and flint lend themselves to direct analysis for silica with, perhaps, minor impurities, *e.g.* limonite.

Ferruginous deposits, of whatever origin, depend for their analyses largely on the amount and manner of combination of iron present in the sample; technique is governed by this factor and each case must perforce be dealt with on its own merits.

Similarly with the carbonaceous group: coals require completely different methods of attack from normal sediments; so do native asphalts; while oil shales provide a problem in combined hydrocarbon determination and silicate analysis which puts them in a class, chemically speaking, on their own.

Phosphatic rocks (organic) are generally exceedingly variable in composition according to source of origin. The approach is normally to an apatite analysis, involving determination of lime, fluorine and phosphate, often plus combined water and other impurities easy of identification with aid of the petrological microscope.

Natural chemical deposits, excluding bedded iron ores and similar deposits, if reasonably pure, are amenable to methods as normally laid down for specific salts or mixtures thereof. Increase in impurities, however, can soon translate what would otherwise be a routine inorganic analysis into one where considerable complexity in composition demands not only chemical, but often more specialized methods of investigation, *e.g.* spectroscopic and/or X-ray techniques (Vol. I, Chs. XI, XIII respectively).

SEDIMENTARY ROCK CONSTITUENTS

Essential minerals present in sediments destined for quantitative chemical analyses may be known and so designated *beforehand*, in which case the analyst proceeds to determine such elements as oxides or *per se* as may be implicit in constitution of the particular rock-type concerned. In different experiments, although certain components of samples in hand may be prognostic, others, including minor accessory minerals, may still remain to be assessed. Again, there is always the unpredictable specimen cropping up when, from a strictly chemical standpoint, initial procedure in analysis is perforce governed by experience and skill of the operator concerned. Regarded from that angle alone, this problem may prove both difficult, obstructive and time-consuming; there is, however, at least a short cut in all such circumstances.

Whatever background information is available, whether mineralogically complete or only partial in detail, preliminary examination of the material to be analysed and by standard petrographic methods is, in our opinion, a *sine quâ non* in rock analysis technique. Even if the sample in hand is a comparatively easily identifiable rock-type, always providing there is sufficient material available, the thin section (consolidated rock), mount (crushed rock, detrital or incoherent sediment), are alike indispensable to procedure, never a waste of time.

Thin sections reveal ultimate mineral composition in advance. Their interpretation under a petrological microscope immediately influences design of chemical analysis, guiding certain obvious determinations which must be made or, on the other hand, by exclusion of suspected but actually non-existent constituents, narrowing down the field of chemical enquiry.

With incoherent materials, petrological examination precedent to chemical operations, is again always worth while. Even finely divided material, natural or synthetic, highly magnified and optically searched, will often betray its identity in the hands of the experienced petrographer, thus directing and facilitating the task of its chemical elucidation.

Further, in this sense, heavy mineral residues prepared from sediments of all descriptions (this applies equally to synthetic materials) in the conventional manner (Chapter III), can afford an immense number of data when minor accessory species are included in the analytical target, *e.g.* complex silicates such as amphiboles, micas, pyroxenes, tourmaline, etc.; simple compounds, *e.g.* rutile, zircon; rare-earth minerals, *e.g.* monazite, thorianite; and trace elements. Especially in the last two categories, if chemical analysis is to proceed to finality, petrographic methods, often with advantage supplemented by spectrographic examination (Chapter XI), are inevitable preliminary stages in these quantitative investigations.

There arise, unfortunately, those infuriating conditions when the amount of sample submitted for analysis is barely large enough for restricted chemical determinations, let alone preliminary microscopical examination. This applies particularly to hand-picked mineral concentrates (under the microscope) or material which, may be, of a different kind, is in exceedingly short supply. Even so, *carefully conserved and manipulated, without mounting in any medium other than air*, a few particles of the powder sample may afford an initial clue to its identity under a petrological microscope, and then be safely returned *in toto* to the analyst without loss or impairing in any way its character or composition, on chemical grounds, in the slightest degree. In other words, a petrographical approach, construed in its widest sense and in accord with relevant methods described in this book, to problems in geochemistry, is emphatically the realistic manner in which to carry out rock analyses where these are involved in such work, not just as specialized technique, but equally important, as a way to establish accurate mineralogical interpretation of results.

Mention has already been made above of the conventional minimum thirteen constituents determined in silicate analysis. A. W. Groves¹ lists these as follows:

SiO ₂	CaO
TiO ₂	Na ₂ O
Al ₂ O ₃	K ₂ O
Fe ₂ O ₃	H ₂ O + 110°C.
FeO	H ₂ O - 110°C.
MnO	P ₂ O ₅
MgO	

Those constituents of sedimentary rocks which *may* be called for in their analyses, additional to the above, are:

¹ *Op. cit.*, p. 28.

CO ₂	F
SO ₃	S
Cl	FeS ₂
C	

When comprehensive analyses are undertaken to include minor accessory minerals, trace elements etc., the list can be considerably extended (see p. 328), but these are the more usual determinations in these categories:

Cr ₂ O ₃	SrO
V ₂ O ₃	CuO
NiO	SnO
CoO	PbO
BaO	ZnO
Li ₂ O	

PREPARATION OF ROCK-SAMPLES FOR ANALYSIS

Chapter II dealt in detail with sampling of sedimentary rocks chiefly from a *geology in the field* standpoint. Here we are concerned with more refined methods of reducing what has been collected in the field, or elsewhere, to such proportions and fineness as must inevitably form basis of the analyst's work. Essence of precision in this matter is to obtain absolutely representative, *uncontaminated* material from bulk by the best means available and with minimum hand-manipulation. Quantity of rock-sample finally available for analysis is obviously a vital factor in its preparation, but this phase of the subject is more conveniently considered separately in sequel (p. 307).¹

Reduction of bulk consolidated rock means first breaking it down into workable size pieces by use of a geological or other type of hammer of appropriate weight; second, proceeding to crush those pieces into fine aggregate; third, their ultimate grinding and pulverizing by suitable processes.

It is clear that in the first phase of breaking rock down, amount of bulk taken will depend on such physical features as its texture, homogeneity in crystallization or mass; also availability of raw material. With a coarsely-crystalline sandstone, *e.g.* Penrith Sandstone (Permian), Cumberland, a larger initial bulk must be taken than, say, with fine-grained Carboniferous Limestone (Pennines) or, by contrast, blue-grey, sticky London Clay, which in any case does not lend itself to crushing in the ordinary sense unless dried.

¹ See particularly H. W. Fairbairn and ors., *A Cooperative Investigation of Precision and Accuracy in Chemical, Spectrochemical and Modal Analysis of Silicate Rocks*, U.S.G.S., Bull. 980, 1951.

Again, procedure is largely governed by amount of raw material submitted. Obviously where a specimen is restricted in size, is difficult of replacement, *e.g.* samples sent from inaccessible places, from limited outcrops, or is subject to circumstances denying supply of more material, the analyst has to fall back on a *modus operandi* which ensures that he makes the best possible use of what he has; that there is no waste in preparation; and, with luck, that he may still have a small portion left for reference or even repeat determinations if such are demanded.

With incoherent materials, both breaking down and crushing operations are seldom necessary if fineness is of the order of $\frac{1}{16}$ -in. particle size or less; such material will be ground down straight away without any other preliminary mechanical treatment. Coarse aggregates, $\frac{3}{16}$ -in. grain size and above, especially in the pebble range, may require the hammer first, but will certainly demand some crushing and final grinding down to powder.

Initial breaking down of bulk rock is either done in the field at time of collection, when the geologist concerned is responsible for producing representative pieces to make up the sample(s) supplied to the laboratory, or it may have to be done inside, when either a rock-splitting apparatus is employed (p. 89) or, more simply, hammering on a specially toughened steel block. One circular pattern in constant use in the author's laboratories has dimensions $7\frac{1}{4}$ in. diameter by $4\frac{1}{4}$ in. height. It can be placed in a tray or on a sheet of clean brown paper on bench or floor, remains perfectly rigid while the rock is hammered and broken down and is, moreover, quite efficient. With a really good hardened steel block (*e.g.* tungsten or nickel steel), it is surprising how well the surface stands up to repeated impact of hammer blows on rock-specimens under treatment. Initial breakdown of rock by hammer should reduce the bulk to at least $\frac{3}{8}$ in. to $\frac{3}{4}$ in. size prior to crushing.

Actual crushing operations vary according to facilities. Where the quantity of broken rock is substantial, the use of some form of mechanical crushing and grinding equipment is often an advantage.

The 'Pulvac' type mill is specially designed for laboratory purposes and operates on the principle of centrifugal action between revolving and stationary crowns, the latter armed with hardened steel beaters, the former fitted with grinding rings. Perforated metal screens from 0.25 mm. and upwards in diameter can be inserted in the mill to give products of predetermined mesh. This mill is capable of dealing successfully with materials as diversified as asphalt, bricks, chalk, china clay, coal, quartz, etc.

Ball mills are also employed for a similar purpose, using porcelain

pots and balls or flint balls. These are usually constructed in 3, 6 or 9 units and are quite efficient with most sedimentary rocks, except perhaps the hard siliceous types.

A more recent newcomer in the field of laboratory mills is the Raymond¹ which employs the principle of impact of swing hammers, the product being classified through varying mesh screens fitted in the base, giving a range from 20-mesh material down to powder. This mill is unsuitable for hard siliceous rocks, *e.g.* quartzite, but it can handle efficiently such substances as hard asphalt, bauxite, calcareous rocks, chalk, clay, coal, diatomaceous earth, fuller's earth, gypsum, iron oxide, kaolin, lignite, mica, pigments, etc.

Another method of crushing broken rock, concrete, etc., to a size suitable for further grinding, is often successfully employed in testing laboratories equipped with a 500 ton (or more) compression machine, such as is used for concrete or rock crushing strength determinations. It is quite practicable to rig up some form of medium (*e.g.* paper) in which the coarsely broken rock-sample is placed and then, after applying the load, to recover the crushing product without loss and in a state ready for final grinding.

For hand-operation, crushing can be effected by use of a steel percussion mortar, a cylindrical receptacle made of specially hardened steel in the bottom of which is placed some of the rock fragments to be crushed; then a closely fitting hardened steel pestle is inserted; the latter is subjected to several heavy blows with a suitable weight hammer and thereafter the crushed material is poured into an appropriate container. The process is repeated until *all* the bulk is reduced to a powder which will pass an I.M.M. 90-mesh sieve² or, better still, a B.S.120-mesh sieve (apertures 0.139 mm. and 0.124 mm. respectively, which means a slightly finer product from the B.S. sieve)³.

The use of iron mortars and pestles, bell-shape, without lip, is common practice in many industrial laboratories. Popular sizes are mortar diameter 6 in. and 10 in.; larger sizes are available but are not recommended for this particular work. Incidentally, the mechanical counterpart of the ordinary iron pestle and mortar is the end-runner type mill used for grinding wet or dry materials. It probably finds somewhat limited use in rock analysis. The 'Diamond' type mortar is also employed where small quantities of material are involved, but its use is strictly limited in primary crushing.

When it comes to final grinding of a rock-product for analysis, use is frequently made of the agate mortar and pestle, although it must be admitted that minus 120 mesh B.S. sieve material will not normally require much further treatment.

¹ International Combustion Ltd., Woburn Place, London, W.C.1.

² A. W. Groves, *op. cit.*, p. 20.

³ Chapter IV, p. 167.

In the forefront of these varied means of making ready rock-powders for chemical analysis, contamination from various implements and apparatus employed to reduce bulk to fine powder is a real problem, fundamentally iron from mills and mortars; silica from certain types of ball mill, perhaps less commonly from agate. Other contaminants are those elements present in alloy steels, *e.g.* manganese, nickel, tungsten, which, in certain specific cases of sedimentary rocks, may have to be considered; the risk here, however, is far less than with igneous and metamorphic types. A. W. Groves discusses these possibilities, with useful practical hints for avoiding infection of this kind, in his valuable work on Silicate Analysis¹. F. R. Ennos and R. Sutcliffe have discussed the 'tendency to use exclusively "diamond steel" percussion mortars for . . . pulverizing the material to be analysed. There are many minerals which can easily abrade agate mortars, and when these occur with other constituents which are more easily powdered their abrasive powers may be serious . . . the abrasion may increase the silica-content of the powder finally obtained. While this may not be regarded as being of importance in the case of many rocks, it . . . cannot be ignored where very accurate estimations of silica are necessary'². In the case of high silica-bearing sedimentary rocks in the arenaceous group, *e.g.* sandstone, quartzite, ganister, etc., it is doubtful whether agate contamination is of serious consequence, unless for some special academic reason the silica content must be returned with a high degree of accuracy. Much the same argument is implied in the argillaceous group. In relatively low silica-bearing types such as normal calcareous sediments, it is most unlikely that, unless the agate utensils have been grossly abused, additional silica derived therefrom will make any really significant difference to the actual silica content of the sample, a remark applying with even more force to organic silica, *e.g.* chert, flint and most representatives of chemical deposits.

MINIMUM QUANTITIES AVAILABLE FOR ANALYSIS

The final sample as prepared for chemical analysis should, if possible, be a minimum of 20 g. for all normal sedimentary rocks. This allows for repeat determinations should such be necessary. With specific, especially rare, minerals, this may not be practicable, particularly when working with a concentrate which has had to be hand-picked under a petrological microscope. In skilled hands

¹ *Op. cit.*, pp. 23-27.

² Chemical Analyses of Igneous Rocks, etc., *Mem. Geol. Surv.*, 1931, p. 154. See also W. F. Hillebrand, G. E. F. Lundell and *ors.*, *op. cit.*

it is possible to carry out determinations of twelve or more essential constituents on far less material than 20 g.; a recent instance in the author's laboratories was 3.7 g. material on which SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , FeO , MgO , MnO , CaO , F , Cl , $\text{H}_2\text{O}+$ and $\text{H}_2\text{O}-110^\circ\text{C}$. were determined with still some to spare; quite a lot can in fact be done even with only 1 g. of powder in some cases (*infra*). Where micro- or semi micro-methods are employed, amounts (mgs.) much smaller than 1 g. of material are involved (see Chapter IX).

In an informative specimen calculation of analysis of a quartz-diorite from Malvern, England, A. W. Groves¹ reports the detailed determination of twenty-five constituents, with final summation of 100.43%, involving the use of a total of 30.5 g. of rock for the analysis. This amount was allocated as follows (constituent determinations in order given):

Main portion, SiO_2 , R_2O_3 , $\text{CaO} + \text{SrO}$, MgO	1.0000 g.
Alkalis, Na_2O , K_2O	0.8000
Ferrous Iron, FeO	0.9982
Total Iron	—
Titania, TiO_2	—
Hygroscopic Water, $\text{H}_2\text{O} - 110^\circ$	2.5748
Total Water	2.7616
Phosphorus, P	1.5763
Manganese and Barium, Mn, Ba	2.1062
Strontia, SrO	—
Carbon dioxide, CO_2	2.0064
Nickel, Ni	2.9909
Fluorine, F	2.0302
Copper Oxide, CuO	2.5285
Chromium and Vanadium, Cr, V	4.9060
Sulphur and Zirconia, S, Zr	2.0691
Chlorine, Cl	2.1806
Alumina, Al_2O_3	—
Total	30.5288 g.

Although the example is igneous and not sedimentary material, it does illustrate the order of amounts of original rock used in different estimations in this particular case and is a guide to how an academic silicate analysis may shape when plenty of material is available.

By sharp contrast, a simpler example, involving far less material in the case of a specimen of crushed and air-elutriated Coal Measure shale, analysed in the author's laboratories², may be quoted. In this instance the total quantity of sample used was 1.2 g. to determine 10 constituents. Allocation of weights of sample taken during the course of the analysis was as follows:

¹ *Op. cit.*, appendices B, C., pp. 325-330.

² *Anal.*: A. H. Clarke, Geochemical Laboratories.

Carbon dioxide	
Loss on ignition	
Silica	
Ferric oxide	0.6 g.
Alumina	
Titanium dioxide	
Calcium oxide	
Magnesium oxide	
Sodium oxide	
Potassium oxide	0.6 g.
Total	1.2 g.

This was the procedure. Loss on ignition was determined by weighing the sample in a platinum boat and heating in a current of air in a tube-furnace at 950°C. At the same time carbon was determined by inserting a soda-lime tube in the furnace outlet and weighing the evolved carbon dioxide. Subsequently, the ignited material was fused with sodium carbonate, and silica, ferric oxide, alumina, titanium dioxide, lime and magnesia determined in the usual way. The alkalis were determined on the separate half (0.6 g.) of the total sample available at the outset.

METHODS OF ANALYSIS (GENERAL)

It is not practicable in available space to give all necessary working details of the analytical methods described. The methods are in general those employed by us for many years past and based mostly on well-tried classical procedures¹. Although a brief description is given of chemical methods of analysis of comparatively rare constituents, it is usually quicker and more satisfactory to determine these by spectrographic rather than chemical analysis, especially if amounts present are very small².

¹ These are collectively covered by the four textbooks cited on page 300: A. W. Groves (1951); W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman (1953); A. Holmes (1923); H. S. Washington (1930), also by W. F. Hillebrand (1919). To these authors we, like other silicate analysts, owe a debt of gratitude for guidance on first principles and applications of this highly specialized branch of inorganic chemistry. Their works, so often quoted throughout relevant literature, including this present chapter, should be available to all students and research workers in this particular field.

A few modifications in standard analytical procedure, devised by past and present chemists on the staff of Geochemical Laboratories, are embodied where appropriate and as extracted from our technical files on Silicate Analysis (H.B.M., A.H.C.).

² L. H. Ahrens, *Quantitative Spectrochemical Analysis of Silicates*, (Pergamon Press, London), 1954; H. W. Fairbairn and *ors.*, *op. cit.*, Part 4.

SEDIMENTARY ROCKS CONTAINING SUBSTANTIAL
SILICA OR SILICATES (ARENACEOUS, ARGILLACEOUS,
SILICEOUS, ORGANIC AND CHEMICAL DEPOSITS)

1. *Standard methods of analysis.*

For determination of the main constituents, approximately 1 g. of sample is used (see however p. 307). This is weighed into a platinum crucible and mixed with sodium carbonate; the amount of sodium carbonate required depends on the basicity of the rock, a good average being eight times the amount of sample taken. The mixture is carefully fused. After cooling the melt, it is extracted with dilute hydrochloric acid and the extract placed in an evaporating dish together with any separated gelatinous silica. The acid extract is evaporated to dryness on a water bath to dehydrate the silica; the residue is then cooled, treated with hydrochloric acid and water, filtered and washed. The filtrate is again evaporated to dryness, followed by treatment with hydrochloric acid and water, filtration and washing. The two filter papers containing silica are placed in a weighed platinum crucible and the silica ignited to constant weight. Silica is then treated with a few drops of sulphuric acid and the crucible filled to approximately half its capacity with hydrofluoric acid.

The hydrofluoric acid is evaporated by placing the crucible on a hot plate in a fume cupboard. After further hydrofluoric acid treatment, the crucible is ignited, weighed and reserved for ignition of the ammonia precipitate (*infra*).

It is important to note that the foregoing procedure for silica determination must be modified if the material analysed contains fluorine in excess of 2%, otherwise silica is lost as SiF_4 during evaporations. Details of a modified method in the presence of excess fluorine may be found in any of the standard text books of silicate analysis¹.

The filtrate from the silica determination is warmed and made alkaline with ammonium hydroxide (1:1); if much manganese is suspected, it is an advantage to add bromine water prior to ammonia, to ensure that the bulk of the manganese appears in the ammonia precipitate; the latter is dissolved in hydrochloric acid, reprecipitated with ammonia and filtered. After washing until free from chlorides, the precipitate is ignited to constant weight in the crucible used for silica determination.

The principal constituents of this ' R_2O_3 precipitate' are usually oxides of iron, aluminium, titanium, manganese and phosphorus; with these, subsequent examination of the precipitate is relatively simple. However, this precipitate may contain oxides of vanadium,

¹ See, for instance, W. F. Hillebrand, G. E. F. Lundell, and ors., *op. cit.*

zirconium, rare earths, nickel, cobalt, copper, if these elements are present in the original sample. Only treatment of precipitates containing iron, aluminium, titanium, manganese and phosphorus will be considered here.

The ignited ammonia precipitate is fused with dry powdered potassium hydrogen sulphate; after cooling it is extracted with water containing a small amount of sulphuric acid. In accurate work, any insoluble matter is filtered off, ignited, weighed and treated with hydrofluoric acid to determine traces of silica. After filtration the water extract is made up to a known volume; an aliquot is taken for determination of iron, titanium and manganese if required.

A convenient method for iron estimation is titration of the solution containing iron with titanous chloride, previously standardized against a solution of known strength containing ferric iron; in this titration, ammonium thiocyanate is added as indicator. This estimation gives total iron in the sample expressed as ferric iron. A separate determination for ferrous iron is necessary in order to obtain the amount of iron actually present in the sample in the ferric state (see p. 312).

If the total amount of titanium in the sample is of the order of 3 to 4%, it is necessary to determine this element by a gravimetric method. In most rocks the amount is small, less than 1%, and titanium can be determined more conveniently by a colorimetric method. To the solution containing titanium, a known amount of sulphuric acid and hydrogen peroxide are added, whence a yellow colour is produced. This colour is matched by preparation of standards containing the same amounts of sulphuric acid and hydrogen peroxide with varying amounts of titanium.

Manganese may be determined on a further aliquot of the fusion extract, although if the amount of sample permits, it is more satisfactory to determine this element on a separate portion; allowance must then be made for any manganese precipitated with calcium and magnesium in calculating the amount in the ammonia precipitate.

Phosphorus also is best determined on a separate portion of the sample (see p. 313).

In the relatively straightforward technique described, amount of alumina is determined by deducting the sum of the iron, titanium, manganese and phosphorus, all expressed as oxides, from total ignited weight of ammonia precipitate.

The combined filtrates from the ammonia precipitation are rendered slightly acid with hydrochloric acid. After warming, oxalic acid is added, followed by ammonia (1:1) until alkaline. Calcium and most of the strontium are precipitated as oxalates.

In accurate work, a reprecipitation of the oxalate should be carried out. After filtration and washing, the oxalate is ignited to constant weight, giving calcium and strontium in the form of oxides. The precipitate should be tested for manganese. If strontium is present it may be estimated by conversion of the ignited oxides to nitrates; dried calcium nitrate is soluble in concentrated nitric acid, whereas strontium nitrate is insoluble.

The filtrate from calcium determination is acidified with hydrochloric acid and evaporated to dryness. The residue is treated with nitric acid to remove ammonium salts and again evaporated to dryness. The resulting salts are then dissolved in water, the solution acidified with hydrochloric acid, and diammonium hydrogen phosphate added, followed by concentrated ammonia. Magnesium is precipitated as magnesium ammonium phosphate. The precipitate is filtered, washed, dissolved in hydrochloric acid and re-precipitated as before. The second precipitate is filtered off and washed, then carefully ignited to constant weight; magnesium is weighed as magnesium pyrophosphate, which may in some cases contain manganese and calcium; these must be determined and the appropriate correction applied.

Other constituents present are best determined on separate portions of the sample.

Alkalis. The sample (about 0.6 g.) is heated with an equal weight of ammonium chloride and eight times its weight of calcium carbonate in a (Lawrence Smith) platinum crucible. After cooling, the mixture is leached with water and filtered; alkalis pass into solution as chlorides. The solution containing alkali chlorides is evaporated to dryness after removal of any calcium in solution and the mixed alkalis weighed as chlorides.

Potassium is determined in the mixed chlorides by conversion to potassium perchlorate and sodium can be determined by difference, unless lithium chloride is present. If lithia is present, it is best estimated on a separate portion of the mixed alkali chlorides by extraction of the lithium chloride with a solvent (e.g. amyl alcohol), finally converting and weighing as lithium sulphate.

Ferrous iron. Approximately 1 g. of sample is weighed in a large platinum crucible, 8 ml. of sulphuric acid (1:1) and 8 ml. of hydrofluoric acid are added and the mixture boiled to decompose the silicates; the crucible and contents are then placed in a beaker containing 200 ml. of a freshly prepared saturated solution of boric acid, well stirred, and ferrous iron in solution titrated immediately with N/20 potassium permanganate.

Water. Hygroscopic moisture is determined by weighing 2 g. of sample into a weighing bottle and drying to constant weight in an oven at 110°C. Total water is determined by weighing 2 g. of

sample into a boat and placing it in a silica tube heated by an electric furnace; a current of dry air is passed through the tube and water evolved is trapped in a weighed absorption tube containing calcium chloride or magnesium perchlorate. In many cases water is not easily removed even if the sample is heated to 900° – 1000°C. , and use of a flux, *e.g.* sodium carbonate, is desirable; if, however, sodium carbonate is employed as flux, then a platinum boat is essential. The amount of combined water is found by deducting hygroscopic water from total water content¹.

Manganese. The method of determining manganese consists essentially of treating the sample (0.2–2.0 g.) with 20 ml. 1:1 sulphuric and 30 ml. hydrofluoric acids in a platinum dish. Contents of the dish are evaporated to fumes, a crystal of potassium nitrate added during fuming and the dish allowed to cool. The contents of the dish are diluted with water, nitric acid added to give 23% by weight of the solution and sodium bismuthate added to oxidize manganese present to permanganate. The permanganate formed is estimated colorimetrically or by titration, according to amount. This method requires modification if certain elements are present with the manganese, *e.g.* cobalt, chromium, antimony.

Phosphorus. The sample is decomposed with hydrofluoric and nitric acids and evaporated to dryness in a platinum dish; two evaporations are usually necessary to ensure complete removal of silica. The residue is dissolved in water and phosphorus is precipitated as ammonium phosphomolybdate, reprecipitated as magnesium ammonium phosphate. This precipitate after filtering and washing is ignited and weighed as magnesium pyrophosphate.

Carbon Dioxide. A weighed amount of the sample is attacked with acid; hydrochloric acid may be used but phosphoric acid is generally considered more satisfactory; carbon dioxide evolved is absorbed in a weighed tube packed with soda-lime.

Carbon. This element is determined in the same apparatus as employed for carbon dioxide. The sample containing non-carbonate carbon is treated with chromic and phosphoric acids to oxidize carbon to carbon dioxide and the evolved gas is absorbed in a weighed soda-lime tube.

Sulphur. The method used for sulphur determination depends on the form in which sulphur is present. Total sulphur is determined by fusion of the sample with sodium carbonate, leaching with water and filtering. Total sulphur as sulphate is determined in the filtrate by precipitation as barium sulphate.

Acid Soluble Sulphates. These are determined by treating the

¹ See C. O. Harvey, Simple Method for Determination of Water in Silicates, *Geol. Surv. Gt. Brit., Bull.* 1, 1939, p. 8.

sample with boiling dilute hydrochloric acid, filtering and precipitating the sulphate in the filtrate as barium sulphate. In a simple case where acid insoluble sulphates are not present, these two determinations are sufficient; sulphur as sulphate is deducted from total sulphur to give the amount of sulphur combined as sulphide; this sulphur content enables sulphides, *e.g.* pyrite (FeS_2), to be calculated.

Chlorine. Total chlorine is determined by fusion of the sample with sodium carbonate and leaching with water. After filtration, chlorine in solution as chloride is determined gravimetrically or turbidimetrically as silver chloride. Acid soluble chlorine is determined by treatment of the sample with boiling dilute nitric acid. Chlorine is determined as silver chloride on the filtrate from acid extraction.

Fluorine. The material is obtained in solution as alkali fluoride by fusion of the powdered rock with a mixture of equal parts of sodium and potassium carbonates, and leaching with water. Silica, alumina and iron oxide are removed by treatment with zinc nitrate, followed by evaporation to low bulk and filtration. Other undesirable elements may have to be removed prior to determination of fluorine, in particular vanadium if present, and final estimation of the former made colorimetrically.

The colorimetric estimation of fluorine is satisfactory if the amount in the sample is less than 2%; it depends on the bleaching effect of fluorine on the yellow colour produced when hydrogen peroxide is added to a solution containing a titanium salt. If the amount of fluorine in the sample is greater than 2%, then a gravimetric estimation must be employed. Several methods are available, determination of fluorine as calcium fluoride or as lead chlorofluoride being probably the most convenient.

Chromium. The powdered sample is fused with sodium carbonate and a crystal of potassium nitrate added to ensure oxidation of the chromium. After cooling, the melt is leached with water, filtered, and the filtrate evaporated to suitable bulk for colorimetric estimation of chromium by comparison with standard chromate solution.

Vanadium. A relatively large amount of powdered sample (5 g.) is fused with sodium carbonate (20 g.) and potassium nitrate (3 g.). The fused mass is leached with water and filtered. Silica and alumina are removed from the solution, and vanadium, together with chromium, molybdenum, arsenic and phosphate, are then precipitated by means of mercurous nitrate. The precipitate is ignited and fused with sodium carbonate, then leached with water and acidified with sulphuric acid; any molybdenum and/or arsenic, if present, are removed by saturating the solution with hydrogen

sulphide. After removal of sulphides by filtration, the solution is boiled to expel hydrogen sulphide, and vanadium estimated by titration of the hot solution with standard potassium permanganate.

Nickel. The powdered sample is decomposed in a platinum dish with sulphuric and hydrofluoric acids and fumed to remove hydrofluoric acid. The contents of the dish are dissolved in water, the solution neutralized, and nickel precipitated by an alcoholic solution of dimethylglyoxime.

Cobalt. The powdered sample is decomposed by fusion with sodium carbonate and silica removed as described in methods for main constituents (p. 310). Iron, alumina, etc., in the filtrate from silica, are removed by a basic acetate separation. Cobalt, together with manganese, nickel, copper and zinc, appear in the filtrate and are precipitated in ammoniacal solution as sulphides. Manganese and zinc are separated by treating the mixed sulphides with dilute hydrochloric acid. In the absence of copper, the residue is dissolved in hydrochloric acid containing bromine water, evaporated to dryness to remove bromine and cobalt precipitated with α -nitroso- β -naphthol and the precipitate filtered, ignited and weighed as cobalt oxide.

Barium. The sample is fused with sodium carbonate and the melt leached with water. After filtration the material insoluble in water is dissolved in hydrochloric acid. Barium is precipitated from this solution by the addition of dilute sulphuric acid and the precipitate is filtered, washed, ignited, then weighed as barium sulphate.

Copper. If cobalt is to be determined in the sample, then copper is removed from acid solution as sulphide prior to precipitation of cobalt. Alternatively, copper may be precipitated as sulphide in the acid filtrate from silica determination. Copper in the copper sulphide is determined colorimetrically or volumetrically according to the amount present.

Tin. The sample is either fused with sodium hydroxide or, if sulphide is present, it is first treated with nitric acid and the residue then fused in order to render the tin in solution. Interfering elements, *e.g.* tungsten, molybdenum, vanadium, must be removed. The solution containing the tin is acidified with sulphuric and hydrochloric acids, then boiled and tin thus reduced to a bivalent state by addition of lead. After cooling, the liquid is titrated with standard iodine solution thereby oxidizing the tin to the quadrivalent state.

Lead. The sample is fused with sodium carbonate, the melt cooled and leached with dilute sulphuric acid. On evaporation to fumes, silica and lead sulphate separate and are filtered off; this precipitate may also contain other insoluble sulphates which must

be removed, as well as silica, prior to final determination of the lead as sulphate.

Zinc. The sample is decomposed by fusion with sodium carbonate and the melt thus obtained is treated as described in the method for determination of cobalt (p. 315). Manganese and zinc are present in the filtrate after treating the mixed sulphides (cobalt, manganese, nickel, copper, zinc) with dilute hydrochloric acid saturated with hydrogen sulphide. Zinc is separated from the manganese by precipitation as sulphide in an acid solution (pH 2-3). The sulphide is dissolved in hydrochloric acid and the zinc finally determined by precipitation with 8-hydroxyquinoline.

Uranium. In recent years many methods for determination of uranium, especially in small amounts in rocks and minerals, have been developed. The initial treatment of the sample will depend upon its nature, but most uranium ores can be decomposed by nitric and hydrochloric acids. Different techniques have been described for final determination of uranium after separation; reduction of uranium to the quadrivalent state and subsequent titration with potassium permanganate; or gravimetric determination as oxide; both are suitable if substantial amounts are present; for small amounts of uranium a colorimetric method is best. Methods developed in the laboratories of the H.M. Geological Survey are described by C. O. Harvey¹.

2. *Rapid methods of analysis*

The standard methods of analysis outlined above are necessarily time-consuming. For many routine purposes, especially in industry, where numerous determinations of the same constituents have constantly to be made, it is possible to employ more rapid methods, use being made of physical instruments and organic reagents.

The Flame Photometer, a comparatively inexpensive instrument (see Ch. XI, p. 394), permits rapid determination of alkalis and calcium. This is particularly useful as a standard method (p. 312) because determination of alkalis is one of the most lengthy of all.

Recently a complete procedure for rapid determination of the oxides normally required in routine silicate analysis has been described by H. Bennett, W. G. Hawley and R. P. Eardley² to which the reader is referred.

3. *Qualitative analysis*

Unless the constituents present in a sample are known with some degree of certainty, it is advisable to apply preliminary tests for possible elements prior to quantitative analysis. For this purpose any comprehensive textbook on qualitative chemical analysis will

¹ *Geol. Surv. Gt. Britain., Bull.* 3, 1951, p. 43 and references cited.

² *Trans. Brit. Ceram. Soc.*, 57, 1958, p. 1.

give details of the tests to be applied for each element¹. If the amount of material is small then the spot tests described by F. Feigl² are invaluable.

CALCAREOUS ROCKS (ORGANIC AND CHEMICAL ORIGIN)

Standard methods of analysis

The weighed sample (1 g.) is dissolved in hydrochloric acid; very few limestones, however, dissolve completely. Any undissolved matter (e.g. quartz) is filtered, ignited, fused with sodium carbonate, the melt dissolved and added to the main filtrate. This filtrate is then evaporated to dryness to dehydrate the silica and analysis for the main constituents proceeds substantially as described in the previous section (p. 310) for silicate rocks.

In the case of many limestones, determination of silica, iron and aluminium oxides, calcium and magnesium oxides will suffice, together with estimation of carbon dioxide and/or loss on ignition.

Carbon dioxide is determined as previously described for silicate rocks (p. 313), except that a smaller sample is taken, say 0.2 g. Loss on ignition is obtained by igniting a weighed portion of the material to constant weight, but this is not usually a desirable procedure because if alkalis or ferrous iron are present, the result will be inaccurate; however, in the case of limestones not containing alkalis or ferrous iron, the loss will normally represent total carbon dioxide and water in the sample, which is generally the aim of the determination.

Other constituents required in calcareous deposits, e.g. alkalis, sulphate, phosphate, can be determined by methods similar in principle to those previously described for silicate rocks (p. 312).

FERRUGINOUS DEPOSITS

(ORGANIC AND CHEMICAL ORIGIN)

These materials can differ considerably in composition; in some cases they will be soluble in hydrochloric or nitric acids, whereas in others the use of a flux, sodium carbonate or potassium hydrogen sulphate, will be necessary to bring the sample into solution.

¹ See particularly:

A. J. Berry, *Qualitative Inorganic Analysis*, 2nd ed. (Univ. Press, Cambridge), 1948.

G. Charlot, *Qualitative Inorganic Analysis, A New Physico-Chemical Approach*, trans. by R. C. Murray, (Methuen, London), 1954.

D. R. Lewis, *Qualitative Inorganic Analysis*, (Univ. Press, Liverpool), 1957.

A. I. Vogel, *Macro and Semimicro Qualitative Inorganic Analysis*, 4th ed. (Longmans, Green, London), 1954.

² *Spot Tests in Inorganic Analysis*, 5th ed., (Elsevier Publishing Company, Amsterdam, etc.), 1958.

If relatively impure, and a complete analysis is required, then procedure is similar to that described for silicate rocks (p. 310). With material containing a high proportion of iron, it is often only necessary to determine total and ferrous iron, both of which can be estimated easily by volumetric methods¹.

CARBONACEOUS MATERIAL (ORGANIC ORIGIN)

Coal. The most important tests normally carried out on coal are essentially physical, in particular calorific value. Ultimate analysis involves determination of carbon, hydrogen, carbon dioxide, nitrogen, sulphur, phosphorus, arsenic, chlorine. These are highly specialized methods, full details of which are given in B.S.1016: 1942².

Analysis of ash from coal is carried out by methods previously described for rocks containing substantial amounts of silica or silicates (p. 310).

Oil Shale. The oil is extracted by means of destructive distillation or in certain cases with solvents, from representative portions of the material; the amount of oil present can be estimated by weighing the sample taken for test before and after distillation and/or extraction. The shale, after removal of oil, can, if required, be analysed by methods previously described for silicate rocks. An examination of the oil itself is difficult and requires considerable experience; methods of analysis applicable to shale-oil are outside the scope of the present chapter³.

Asphalt. Native Asphalts consist normally of bitumen intimately mixed with siliceous or calcareous matter. The amount of bitumen is estimated by extracting a known weight of the material with a solvent (carbon disulphide or trichloroethylene); the residue is dried and reweighed; the difference gives the weight of bitumen (see Ch. VII, p. 261). It is possible in many cases by a relatively complicated procedure, to recover the bitumen in order that its physical characteristics may be determined⁴. The mineral residue, after extraction of bitumen, is analysed according to its nature by methods previously described for siliceous or calcareous materials.

¹ See refs. to textbooks, p. 300.

² B.S.1016: 1942. British Standard Methods for the Analysis of Coal and Coke. See also B.S.1016: 1957 parts 1-5; 1958, part 6; 1959, parts 7, 8, 11, 12, and 1960, part 9.

³ The Oil-Shales of the Lothians, (*Mem. Geol. Surv., Scotland*), 1927, Part 3, p. 158.

V. C. Alderson, *The Oil Shale Industry*, (F. A. Stokes, New York), 1920.

H. Abraham, *Asphalts and Allied Substances*, 5th ed., (Van Nostrand, New York), 1945, Chs. 12 and 16.

⁴ B.S.598: 1958, part 8.

PHOSPHATE DEPOSITS (ORGANIC ORIGIN)

Analysis of these materials can be complicated and it is only possible here to consider a simple phosphate rock.

A weighed portion of the sample is digested with nitric acid; any insoluble matter is filtered off, ignited, fused with sodium carbonate, extracted with dilute nitric acid and added to the main solution. This is evaporated to dryness to dehydrate the silica; the residue is wetted with nitric acid, taken up with water and filtered, the insoluble silica ignited and weighed. The whole, or an aliquot of the filtrate from the silica, is used for determination of phosphorus. This is first precipitated as ammonium phosphomolybdate and finally converted to and weighed as magnesium pyrophosphate, as previously described (p. 313). Other constituents, notably calcium, are best determined on separate portions of the sample. Alternative methods are available, designed specifically for this type of rock.¹

SALINE DEPOSITS (CHEMICAL ORIGIN)

Providing saline deposits are relatively pure substances and therefore completely soluble in water or acid, analysis is a comparatively simple matter; individual determinations can be made, without any separations, by methods similar to those already described. In many cases, however, saline deposits are not single salts; if this is suspected, qualitative tests must be made to ascertain composition; thereafter experience alone can guide the separations necessary in order to analyse the sample quantitatively.

METHODS OF ANALYSIS (SPECIFIC)

A. DETERMINATION OF FREE SILICA

1. *Chemical methods*

The various chemical methods extant all depend upon decomposition and removal of minerals associated with free silica in the rock. It is rarely possible to effect a really clean separation; either quartz is lost by solution in the reagents employed or certain minerals which are present are resistant to attack.

One method capable of giving reasonably accurate results in many cases, is a modification of the Selvig² procedure by A. Shaw. In this method 5 g. of material previously ground to pass the 60-mesh I.M.M. sieve (equiv. B.S. mesh) are treated with dilute hydrochloric acid; after boiling and allowing to settle, supernatant liquid is siphoned off and the residue treated with 1:1 sulphuric acid. Next, boiling until copious fumes are evolved, cooling, diluting with water

¹ A. W. Groves, *op. cit.*

² *Carnegie Inst. Tech. Min. and Met. Invest., Bull. 21, 1925.*

and allowing to settle, the supernatant liquid is again siphoned off, the sulphuric acid treatment being repeated. The decomposition products are then removed by treatment with a solution containing 10% sodium carbonate and 1% sodium hydroxide, then boiling concentrated hydrochloric acid and finally with the alkaline solution once more. The residue is boiled with concentrated hydrochloric acid, diluted with an equal quantity of water, filtered off, ignited and weighed. This residue contains quartz and any undecomposed minerals. A. Shaw¹ assumed that undecomposed material was feldspar and corrected for this by determining the alumina content of the residue. The weight of alumina multiplied by 5.41 gives the equivalent weight of potash feldspar and this, deducted from the total residue, gives the amount of free silica.

The above method was employed by D. Hicks and G. Nagelschmidt² in their examination of material from the South Wales coal mines and results were in good agreement with free silica (based on mineralogical compositions) calculated from chemical analyses. As the undecomposed mineral was known to be mica, not feldspar, a correction factor of 2.79 was employed in this case.

Similar chemical methods with varying reagents for attacking the material have been described by S. R. Rabson³, A. Knopf⁴, W. R. Line and P. W. Aradine⁵ and L. J. Trostel and D. J. Wynne⁶. The last method was examined critically by W. Cumming, P. B. Dempster and P. D. Ritchie⁷. In this, a finely ground sample of the material to be analysed is fused with potassium pyrosulphate, leached with water and the mixture thus obtained extracted with caustic soda solution. The solid residue is filtered off and washed with water and hydrochloric acid; this residue should be quartz. It is known, however, that feldspar is resistant to this treatment and, if present, a correction has to be applied in order to obtain the true weight of quartz.

2. Differential thermal analysis

This form of analysis can be used for identification of many minerals (see Vol. II, Ch. III, for further details and references). It is useful in the case of free silica because it permits differentiation of various forms of crystalline silica (*i.e.* quartz, tridymite

¹ *The Analyst*, **59**, 1934, p. 446.

² *Chronic Pulmonary Disease in South Wales Coal Miners. II. Environmental Studies*, (H.M.S.O.), 1943, p. 153.

³ *Journ. Chem. Soc. S. Africa*, **45**, 1944, p. 43; **46**, 1945, p. 160.

⁴ *Public Health Report*, Washington, **48**, 1933, p. 183.

⁵ *Ind. Eng. Chem. Anal.*, **9**, 1937, p. 60.

⁶ *Journ. Amer. Ceram. Soc.*, **23**, 1940, p. 1918.

⁷ *Journ. Appl. Chem.*, **2**, 1952, p. 658.

and cristobalite)^{1,2}. These three forms of crystalline silica, like some other minerals, undergo reversible transformations when heated or cooled through certain temperature ranges; one manifestation of these transformations is absorption or evolution of heat. The material to be tested is heated or cooled together with a similar sample of inert material (*e.g.* calcined alumina). The temperatures of both samples are taken during heating or cooling by means of thermocouples. The temperature differential is plotted against actual temperature and the points at which peaks occur in the curve are indicative of specific minerals; the curves can also be used to estimate the amount of such minerals present.

3. Miscellaneous physical methods

Analysis of silicates by chemical methods is a time-consuming operation, if results of a high order of accuracy are required. In recent years, increasing attention has been given to the use of physical instruments to facilitate such analysis.

The most useful is the Spectrograph (see Ch. XI). This can be used for qualitative and quantitative work and is particularly valuable in determination of elements present only in traces. L. H. Ahrens³ and co-workers have devised methods for complete analysis of silicates by spectrographic methods; by means of three to seven separate operations, some thirty-five elements can be determined.

The Flame Photometer has already been mentioned (p. 316) (see also Ch. IX, p. 394) and is now a firmly established technique for determining alkali and other metals accurately and expeditiously. In this instrument, a solution containing the alkali or other metals is sprayed into a flame; the characteristic spectrum lines emitted can be measured separately by a photoelectric cell, after interposing suitable filters. It is necessary to calibrate the instrument beforehand with known amounts of the metals to be determined.

The Spectrophotometer (Ch. IX) is a comparatively expensive piece of apparatus. In using this instrument, light of a suitable known wavelength is passed through a solution containing the element to be determined and the amount of light absorbed is measured. By reference to a previously-prepared calibration curve it is possible to estimate the amount of the element being

¹ A. L. Roberts, *A Positive Method for the Determination of Free Silica in Dusts—Dust in Industry*, *Soc. Chem. Ind.*, 1948, p. 169.

² R. W. Grimshaw, A. Westerman and A. L. Roberts, *Trans. Brit. Ceram. Soc.*, **47**, 1948, p. 269.

³ *Quantitative Spectrochemical Analysis of Silicates*, (Pergamon Press, London), 1954. See also H. W. Fairbairn and *ors.*, *U.S.G.S., Bull.* **980**, 1951, Part 3, p. 25.

determined. Recent work in H.M. Geological Survey Laboratories has demonstrated that spectrophotometric methods can be used with advantage in silicate analysis¹.

CALCULATIONS

With exception of minerals and rocks of relatively simple composition, it is rarely possible to calculate mineral constituents directly from a chemical analysis alone. A knowledge of the minerals actually present in the sample under investigation can best be obtained from a thorough petrological examination, preferably prior to all the chemical work (p. 302). Armed with this information sedimentary rocks, at least, normally present few difficulties in allocation of oxides determined by analysis to the relevant minerals involved; interpretation of analytical results in terms of standard formulae for minerals of comparatively simple constitution is generally straightforward; in cases of more complex substances, e.g. clay minerals, empirical formulae may prove helpful, but X-ray analyses must inevitably supplement such procedure if a reasonably accurate assessment of total mineral composition of the rock is to be realized.

In the realm of igneous rock studies one method of mineralogical interpretation of chemical analysis is by calculation of the *Norm* 'a term applied to the chemical composition of an igneous rock expressed in terms of standard "normative" mineral molecules calculated from the composition as stated in terms of oxides; contrasted with the *Mode*, which is the actual mineral composition, stated quantitatively'². When this procedure can be satisfactorily followed it automatically acts as a check on the chemical analysis, but here again a preliminary petrological examination of the material concerned is a *sine quâ non* to accuracy, since calculation of the norm alone does not give either actual mineral composition or mode.

Further, although the norm is calculated on a weight basis, the mode, as established petrologically, is of necessity on a volume basis; hence adjustments in calculations must be made accordingly.

Practice with calculations of the norm, according to the principles laid down for igneous rocks³, is exceedingly good drill for interpretation of mineral composition from chemical analyses, and such reasoning applied to sedimentary rocks, even if more

¹ *Summary of Progress, Geol. Surv. Great Britain*, 1958, p. 51.

² A. Holmes, *The Nomenclature of Petrology*, (Murby, London), 1928, p. 167; also W. Cross, J. P. Iddings, L. V. Pirsson and H. S. Washington, *Quantitative Classification of Igneous Rocks*, (Chicago), 1903.

³ A. Holmes, *Petrographic Methods and Calculations*, (Murby, London), 1923, Pt. III.

A. W. Groves, *Silicate Analysis*, 2nd ed. (Allen & Unwin, London), 1951.

restricted in scope, at least facilitates understanding of the significance of the chemist's 'oxides' and their translation into mineralogical nomenclature which everyone can understand. For more detailed information on this aspect of the subject, the reader should consult the references below¹.

We may usefully conclude this section with two examples of the mineralogical calculation and interpretation of sedimentary rocks. Further examples of calculations will be found later in this chapter, in the section on Type Analyses.

Example I. Coal Measure Sandstone, Fauldhouse, Linlithgowshire.

Chemical Analysis²

Calculated Mineral Composition

SiO ₂	80.88	Quartz	68.3	SiO ₂ *	
Al ₂ O ₃	9.80	Illite	25.7	K ₂₋₃ Al ₁₁ Si ₁₂₋₁₃ O ₃₅₋₃₆	
				(OH) ₁₂₋₁₃	
Fe ₂ O ₃	2.36	Ilmenite	1.2	FeO . TiO ₂	
MgO	0.31	Apatite	0.1	Ca ₄ (CaF)(PO ₄) ₃	
CaO	0.20	Zircon	0.1	ZrO ₂ . SiO ₂	
Na ₂ O	0.38	Limonite & }		{ Fe ₂ O ₃ . nH ₂ O + MnO ₂	
K ₂ O	1.13	Mn as	2.5		
H ₂ O + 105°C.	2.60	Pyrolusite			
H ₂ O - 105°C.	0.68	Calcite	0.3	CaCO ₃	
TiO ₂	0.65	Magnesite	0.7	MgCO ₃	
P ₂ O ₅	0.03	Siderite	1.0	FeCO ₃	
MnO	0.12				
CO ₂	0.85	Total %	99.9		
ZrO ₂	0.05				
FeS ₂	nt. fd.				
NiO	}				
CoO		nt. fd.			
Li ₂ O		nt. fd.			
C		nt. fd.			
Total %	100.04				

* Formulae used in calculation by present authors.

In this example, an impure Coal Measure sandstone containing argillaceous matter, calculation proceeded as follows:

- All the Al₂O₃ is calculated to illite. This takes care of alkalis together with some of the silica and water +.
- All TiO₂ is calculated to ilmenite, which requires some of the iron (FeO was not determined in this analysis).

¹ A. Holmes, *Petrographic Methods and Calculations*, (Murby, London), 1923, Pt. III.

A. W. Groves, *Silicate Analysis*, 2nd ed. (Allen & Unwin, London), 1951.

² Analyst: G. A. Sergeant. See Table 7, Analysis IV, p. 333.

- (c) The P_2O_5 is calculated to apatite which requires some of the calcium (F was not determined in this analysis).
- (d) ZrO_2 is calculated to zircon which requires a small amount of silica.
- (e) All silica remaining after satisfying requirements of illite and zircon is 'free' as quartz.
- (f) Remaining CaO and the MgO are calculated to carbonates, involving the CO_2 ; residual CO_2 is allocated to siderite, involving some of the iron.
- (g) Finally, the residual amount of Fe_2O_3 , with all remaining water +, is expressed as limonite with the associated MnO as pyrolusite.

Example II. 'Cornstone'¹, Lower Old Red Sandstone, (Ditton Series), Stanton Lacey, nr. Ludlow, Salop.

*Chemical Analysis*²

Calculated Mineral Composition

SiO ₂	6.03	Quartz	4.5	SiO ₂ *	
Al ₂ O ₃	1.33	Mica K	2.0	(K, Na) ₂ O . 3Al ₂ O ₃	
Fe ₂ O ₃	0.23	Mica Na	1.4	6SiO ₂ . 2H ₂ O	
FeO	0.17	Apatite	0.3	Ca ₄ (CaF)(PO ₄) ₃	
MgO	1.46	Ilmenite	0.2	FeO . TiO ₂	
CaO	50.08	Barite	<0.1	BaSO ₄	
Na ₂ O	0.11	?Kieserite	0.1	MgSO ₄ . H ₂ O	
K ₂ O	0.24	Limonite &			
H ₂ O + 105°C.	0.68	Mn as	1.4	{ Fe ₂ O ₃ . nH ₂ O + MnO ₂	
H ₂ O - 105°C.	0.27	Pyrolusite			
TiO ₂	0.09	Calcite	89.2	CaCO ₃	
P ₂ O ₅	0.12	Magnesite	3.0	MgCO ₃	
MnO	0.25				
CO ₂	39.22	Total %	102.1†		
Total S	0.03				
BaO	0.02				
Total %	100.33				

* Formulae used in calculation by present authors.

† All the above mineral percentages can only be regarded as approximations; it sometimes happens, as in this example, that calculations of mineral composition deviate from the theoretical 100% by 1 or even 2%. For all practical purposes, however, this is of minor significance. (See D. Hicks and G. Nagelschmidt, Chronic Pulmonary Disease in South Wales Coalminers, II. Environmental Studies, *Med. Res. Council, Spec. Rep.* 244, 1943, pp. 164, 165.)

¹ 'A term applied to the concretionary and other limestone masses associated with the Old Red and the New Red Sandstone formations. Their presence increases the fertility of the soil derived from the formations in which they occur and hence the name.' A. Holmes, *The Nomenclature of Petrology*, 2nd ed., (Murby, London), 1928, p. 69. 'Cornstones' are generally chemical precipitates laid down in lakes under continental conditions.

² *Sum. Prog. Geol. Surv. Gt. Brit.*, 1956, p. 57. *Anal.*, A. D. Wilson and P. Coombs.

In this example, we are dealing with a limestone, most probably of chemical origin, containing finely-divided clay matter, and some free detrital quartz. The calculation proceeded as follows:

- (a) All K_2O and Na_2O were calculated to mica, the remainder of the silica reported as quartz.
- (b) All P_2O_5 calculated as apatite, remainder of CaO allocated to carbonates (calcite, magnesite).
- (c) All TiO_2 calculated to ilmenite, small amount of FeO remaining grouped with limonite.
- (d) BaO calculated to sulphate and remaining sulphur calculated to ?kieserite; remaining MgO calculated to magnesite.
- (e) All Fe_2O_3 together with FeO , water and manganese (as pyrolusite) grouped together.

MINERALOGICAL INTERPRETATION OF OXIDES FOUND BY CHEMICAL ANALYSIS

In the foregoing lists of major and minor sedimentary rock constituents (p. 303), their individual significance may be interpreted as follows:

- | | |
|-----------|---|
| SiO_2 | as quartz, chert, flint, chalcedonic and other forms of silica; silicate minerals, <i>e.g.</i> clays. |
| TiO_2 | as ilmenite and other titaniferous minerals. |
| Al_2O_3 | as feldspar, mica and clay minerals, closely associated with silica in many silicate minerals. |
| Fe_2O_3 | in ferromagnesian silicates, sedimentary iron ores. |
| FeO | in varied silicates, sedimentary iron ores. |
| MnO | as $MnCO_3$ (rhodochrosite) in metasomatic replacements of limestone; as sedimentary or residual manganese oxides, <i>e.g.</i> MnO_2 (pyrolusite), Mn_2O_3 (braunite), hydrated oxide with Ba and K (psilomelane or wad). |
| MgO | in ferromagnesian silicates, dolomitic limestone; as $MgCO_3$ (magnesite) replacing dolomite and limestone. |
| CaO | as calcite ($CaCO_3$) associated with many sedimentary rock-types, including limestone and dolomitic limestone; in pyroxenes and amphiboles as minor heavy accessory minerals in detrital deposits. |
| Na_2O | as feldspar; soda-bearing ferromagnesian accessory minerals; as rock-salt associated with sedimentary deposits; in chemical deposits. |

K_2O	as felspar; in saline-bearing deposits.
H_2O	in micas and clay minerals; as hydrated oxide of iron (limonite); combined ($H_2O+105^\circ C.$) to some extent practically universal in sedimentary rocks; uncombined ($H_2O-105^\circ C.$), haphazard, according to nature and porosity of rock.
P_2O_5	as $Ca_5F(PO_4)_3$, fluor-apatite; $Ca_5Cl(PO_4)_3$ chlor-apatite; rock phosphate (phosphorite), phosphatic limestone, coprolites, bone beds.
CO_2	in calcareous rocks of all kinds; carbonate minerals; weathered sedimentary rocks; bedded ironstones; as $FeCO_3$ in sedimentary siderites.
SO_3	in gypsum-bearing sediments; as $SrSO_4$ (celestite) in sedimentary deposits and as replacement mineral in limestones.
Cl	in rock-salt; chlor-apatite.
C	as carbonaceous matter of organic origin in many sedimentary deposits.
F	as CaF_2 (fluorite) in limestones and other sediments; fluor-apatite; accessory micas; fluorite as cementing medium in certain sandstones (<i>e.g.</i> Trias, Elgin, Scotland); bones.
S	as FeS_2 (pyrite) and other sulphur-bearing minerals in sediments, <i>e.g.</i> detrital pyrrhotite.
FeS_2	as pyrite, ubiquitous in sediments of all kinds.

It may be further noted in connexion with the list of accessory minerals (p. 304), that of the elements sought and expressed as oxides, the following data are significant: Cr_2O_3 in detrital deposits usually means chromite ($FeCr_2O_4$) derived from ultrabasic igneous rocks; V_2O_3 occurs as patronite in certain native asphalts or as motttramite $4(PbCuVO_4OH)$, *e.g.* Triassic sandstone, Alderley Edge, Cheshire. *Nickel* and *cobalt* are rarely determined in sediments except where the former occurs as millerite (NiS) in nodules in clay-ironstone, *e.g.* South Wales, and the latter may be present as smaltite ($CoAs_2$) or cobaltite ($CoAsS$), in alluvial deposits derived from cobaltiferous ultrabasic igneous rocks. *BaO* represents barium present as $BaSO_4$ in barite-bearing sediments, *e.g.* Triassic sandstone, Elgin, and Hemlock Stone (Bunter), of Nottingham, where it constitutes the cementing medium of quartz grains. Apart from known lithium-bearing micas released by weathering of granite-pegmatites and so incorporated in certain

detrital deposits, Li_2O (lithia) is determined in spodumene-bearing sands ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$), *e.g.* Dublin¹. The presence of celestite (SrSO_4) in sedimentary rocks, *e.g.* Triassic sandstone, Yate, Gloucestershire², leads to determination of strontium as SrO in such cases; CuO , as thus expressed, usually means presence of chalcopyrite (CuFeS_2) as in some coals, chalcocite (Cu_2S) nodules in sandstones, *e.g.* Oklahoma, U.S.A., erubescite (Cu_5FeS_4) in sedimentary copper deposits, *e.g.* Kupferschiefer, Mansfield, Germany. SnO_2 , cassiterite, occurs in alluvial and other detrital deposits in practically all tin-bearing regions in the world; occurrences in sediments in this country are listed elsewhere³. PbO normally represents lead present as galena (PbS) and found associated with Fuller's earth, *e.g.* Redhill, Surrey, or Triassic sandstone, *e.g.* Alderley Edge, Cheshire; otherwise with many Carboniferous Limestone deposits. Zn , as sphalerite (ZnS), and expressed as the oxide, is a frequent associate of galena and is often returned as ZnO in analyses of Fuller's earth from different localities in England.

REPORTING ANALYTICAL RESULTS

There is no universally-accepted method of reporting results of rock analyses in a particular vertical sequence of constituents, but as far as the commoner oxides are concerned, for geological purposes in interpreting mineralogical constitution and in cases where calculation of the norm of the rock is involved (igneous rocks), the minimum thirteen constituents (p. 303) do have some claim to priority of place. 'Petrographers now demand, with considerable reason, an arrangement "which shall bring the essential chemical features—both the percentage figures and the molecular ratios—prominently and compactly before the eye, so that the general chemical character and the relations of the various constituents may be seen at a glance" '⁴.

Sequences according to three leading authorities are given on page 328. It will be observed that there are differences in order, number and nature of constituents envisaged by the respective authorities in their statements. In general, with sedimentary rocks, the number of constituents determined to completion and so reported, even in comprehensive academic analyses, is far less on average than in the case of igneous or metamorphic rocks.

¹ Vol. II, Ch. I.

² *Ibid.*, p. 72.

³ *Ibid.*, p. 71.

⁴ W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, (Wiley, New York), 1929, p. 658, quoting H. S. Washington, *The Statement of Rock Analyses*, *Amer. Journ. Sci.*, 10, 1900, p. 61.

*A. W. Groves*¹

SiO₂
 TiO₂
 Al₂O₃
 Fe₂O₃
 FeO
 MnO
 MgO
 CaO
 Na₂O
 K₂O
 P₂O₅
 H₂O + 110°C.
 H₂O - 110°C.
 CO₂
 ZrO₂
 F
 Cl
 S
 Cr₂O₃
 V₂O₃
 NiO
 BaO
 SrO
 CuO
 Li₂O

*F. R. Ennos*²*R. Sutcliffe*

SiO₂
 Al₂O₃
 Fe₂O₃
 FeO
 MgO
 CaO
 Na₂O
 K₂O
 H₂O > 105°C.
 H₂O < 105°C.
 TiO₂
 P₂O₅
 MnO
 CO₂
 ZrO₂
 B₂O₃
 SO₃
 Cl
 F
 S
 FeS₂
 Fe₇S₈
 Cr₂O₃
 V₂O₃
 NiO
 CoO
 BaO
 SrO
 CuO
 SnO
 PbO
 ZnO
 Li₂O
 C
 Org. H

*W. F. Hillebrand*³*G. E. F. Lundell*

SiO₂
 Al₂O₃
 Fe₂O₃
 FeO
 MgO
 CaO
 Na₂O
 K₂O
 H₂O (+ 105°-110°C.)
 H₂O (- 105°-110°C.)
 CO₂
 TiO₂
 ZrO₂
 P₂O₅
 SO₃
 Cl
 F
 S (FeS₂)
 Cr₂O₃
 V₂O₃
 NiO
 CoO
 CuO
 MnO
 SrO
 BaO
 Li₂O
 C
 NH₃

The above lists must therefore be regarded merely as theoretical academic possibilities. In the authors' experience of *industrial* analyses of sedimentary rocks, total constituents determined to conventional summation, tend to range from 12 to 15 with high-silica and silicate types, with only very occasional extensions up to, say, 20; with calcareous rocks, essential components sought may total less than 6 and yet, plus loss on ignition, give reasonable summation. It is normally only within the sphere of pure geochemical research that the list of constituents reported *may* approach one

¹ *Op. cit.*, p. 330.² *Op. cit.*, p. 161.³ *Op. cit.*, p. 659.

of the above sequences and then it is usually a sedimentary silicate analysis, not organically-derived rocks.

Incidentally, a blank or dash (—) in the statement of analysis may mean anything. It can imply that the particular constituent was not determined; is present in the rock but not separated from anything else; or is absent: in other words a blank means 'no information available'. This ambiguity generally only arises where a series of analyses by different analysts are blocked together for comparative purposes and publication. More precisely, *n.d.* at least indicates that the constituent has not been detected, likewise *nil* is a definite statement of its non-existence in the sample concerned; *nt. fd.* suggests that it was looked for but wanting; the word trace or sometimes symbol 0.00 implies that quantity present is less than 0.01%.

As regards summation, limits stated by A. W. Groves¹ 99.75 to 100.50 are generally acceptable. As he points out, anything lower than 99.75 implies non-determination of certain constituents present in the rock; anything more than 100.50 points to incomplete washing and ignition of precipitates. In many cases, however, especially in industrial analyses where only certain constituents are required and chemical examination is partial, any summation is of little practical value and best omitted altogether from the report.

In the author's laboratories it has always been the custom to follow United Kingdom Geological Survey procedure as regards reporting results; this plan is adopted in type-analyses quoted below.

TYPE ANALYSES OF SEDIMENTARY ROCKS

In this section is quoted a series of published and some unpublished analyses of well-known sedimentary rocks, selected as far as possible to illustrate similar types from different British stratigraphical horizons, with occasional overseas examples by way of contrast. Each analysis is adjusted to a common framework of statement in terms of U.K. Geological Survey's order of constituents (p. 328). Arrangement of examples of these rocks together with their appropriate symbols are in accordance with the Classification of Sedimentary Rocks first drawn up by the author in 1940², now included in Vol. II, Ch. II, of the present work. Published analyses are authenticated by full references to original literature and include the name(s) of the analyst(s) concerned in each case where this information is catalogued; analyses carried

¹ *Op. cit.*, p. 37.

² *Sedimentary Petrography*, 3rd ed., (Murby, London), 1940, p. 360.

out in the author's laboratory are designated 'Geochemical Laboratories'.

In the first group (A) MECHANICAL ORIGIN, examples chosen include the following rock-types:

- A2. Arenaceous: Sand (A2.1); Sandstone (A2.1); Quartzite (A2.4) and Gneiss (A2.5).
- A3. Argillaceous: Clay (A3.1) and Fireclay (A3.2); Fullers' Earth (A3.3), Mudstone (A3.8) and Shale (A3.9).

The group midway between Argillaceous (A3) and Calcareous (B1) and designated (AB) is represented thus:

- AB. Calcareo-Argillaceous: Marl (AB.1) and Calcareous Shale (AB.2).

The group comprising rocks of Organic Origin (B) is represented by the following examples:

- B1. Calcareous: Limestone (B1.1); Dolomitic Limestone (B1.2) and Chalk (B1.5).
- B2. Siliceous: Chert, Flint (B2.1) and Diatomite (B2.3).
- B3. Ferruginous: Bedded Iron Ores (B3).¹
- B4. Carbonaceous: Coal (B4.3), Oil-Shale (B4.5) and Asphalt (B4.6).
- B5. Phosphatic: Phosphate (B5.)

Rocks of Chemical Origin (C) are represented by:

- C1. Calcareous: Dolomite (C1.2).
- C2. Ferruginous: Bedded Iron Ores (C2.1).
- C4. Saline: Chloride (C4.1) and Sulphate (C4.2).

SAND (A2.1).—In true silica sands, quartz, occasionally feldspar, frequently limonite or hematite, are essential constituents; in the purer white and 'silver' types, SiO_2 may be returned as high as 99%. With decreasing purity, percentage of Al_2O_3 tends to rise, indicative of presence of feldspar or, more often, of clay substance (especially if $\text{H}_2\text{O}+105^\circ\text{C.}$ is of the order of 1% or more); so also does Fe_2O_3 . The average silica sand falls within the range 75–95% SiO_2 . With a total silica content of 75% or less, the so-called 'sand' is probably more akin petrologically to silt or similar fine-grained sediment. There is, in fact, a progressive fall in SiO_2 with decreasing particle size; where the latter is less than 0.1 mm., then less than 75% SiO_2 is likely, falling to below 50% in 0.01 mm. and finer material.

Heavy mineral sands ('black sands', etc.) are, of course, exceptional occurrences of naturally-concentrated mineral species of relatively high specific gravity; from a chemical standpoint they constitute special cases.

¹ See also under Chemical Deposits.

Economically, sand used for glass-making should have a minimum SiO_2 content of 98%; for best glass, 99.5%¹. Sand used for refractory purposes (siliceous bricks, etc.) should be within 90–95% SiO_2 ; for moulding sands, the SiO_2 content usually ranges from 85% (with natural bond) to 95% (where the sand may have to be artificially bonded).

TABLE 6
ANALYSES OF SAND (A2.1)

CONSTITUENT	I	II	III	IV	V	VI	VII
SiO_2	98.17	96.20	86.11	90.30	84.86	87.14	86.47
Al_2O_3	0.71	1.36	5.29	4.51	6.69	5.89	4.96
Fe_2O_3	0.02	0.49	2.45	1.02	1.08	1.00	2.58
FeO	—	0.12	0.29	0.21	0.35	0.29	0.29
MgO	0.07	0.18	0.47	0.23	0.43	0.41	0.37
CaO	0.11	0.13	0.40	0.15	0.29	0.25	0.26
Na_2O	0.02	0.12	nil	0.12	0.40	0.14	0.12
K_2O	0.09	0.66	0.95	0.75	3.41	2.95	0.47
$\text{H}_2\text{O} + 105^\circ\text{C.}$	—	0.44	2.26	1.72	1.21	1.00	2.44
$\text{H}_2\text{O} - 105^\circ\text{C.}$	—	0.15	1.31	0.52	0.55	0.55	1.54
TiO_2	0.42	0.15	0.34	0.31	0.40	0.18	0.40
P_2O_5	—	0.03	0.08	—	0.09	0.08	0.09
MnO	—	tr.	tr.	—	0.01	0.02	tr.
CO_2	—	nil.	nil	—	nil	nil	nil
ZrO_2	—	—	tr.	—	tr.	0.02	nil
SO_3	—	nil	0.03	—	nil	0.03	nil
Cl	—	tr.	—	—	tr.	tr.	tr.
BaO	—	tr.	nil	—	0.04	0.03	tr.
Loss on ignition	0.41	—	—	—	—	—	—
Totals (%)	100.02	100.03	99.98	99.84	99.81	99.98	99.99

I Refractory Sand (in pockets of Carb. Ls.), Post-Glacial (Triassic material), Newhaven, Derbyshire. P. G. H. Boswell, *Brit. Res. Refractory Sands*, 1918, p. 127. *Anal.* H. F. Harwood and A. A. Eldridge.

II Glacial Sand, Ipswich. P. G. H. Boswell, *op. cit.*, p. 98. *Anal.* H. F. Harwood and A. A. Eldridge.

III Moulding Sand, 'Cornish Red', Pliocene, St. Erth, Cornwall. P. G. H. Boswell, *op. cit.*, p. 131. *Anal.* H. F. Harwood and A. A. Eldridge.

IV Moulding Sand, Upper Estuarine Series (Lower Oolites), Huttons Ambo, near Malton, Yorkshire. *Mem. Geol. Surv., Min. Res.*, XVI, 1920, p. 75. *Anal.* E. G. Radley.

V Moulding Sand, Upper Bunter (Trias), Hockley, Birmingham. P. G. H. Boswell, *op. cit.*, p. 156. *Anal.* H. F. Harwood and A. A. Eldridge.

VI Moulding Sand, Lower Bunter (Trias), Heck, Yorkshire. P. G. H. Boswell, *op. cit.*, p. 149. *Anal.* H. F. Harwood and A. A. Eldridge.

VII Moulding Sand, 'Belgian Yellow', Pliocene, Mons, Belgium. P. G. H. Boswell, *op. cit.*, p. 62. *Anal.* H. F. Harwood and A. A. Eldridge.

¹ P. G. H. Boswell, *British Resources Sands and Rocks used in Glass-Making*, 2nd ed., (Longmans, Green, London), 1918, p. 41.

SANDSTONE (A2.1).—The average sandstone generally yields 75–85% total silica. A composite analysis of 253 sandstones revealed 78.66% SiO_2 ¹ (quoted in Table 7 below). B. Mason², quoting F. J. Pettijohn, gives 78.33% for a composite of 12 sandstones which, according to F. W. Clarke³, is average silica composition for sandstone in the lithosphere as a whole. A composite analysis of 371 sandstones used for building purposes (by H. N. Stokes, quoted by F. W. Clarke⁴) gave 84.86% SiO_2 .

On the other hand, sandstones (silica rocks) suitable for employment in manufacture of refractories, must necessarily have a much higher total SiO_2 content than normal. A mean of 42 British examples of sandstones (silica rocks) analysed by the Geological Survey⁵ is 94.73%.

As with incoherent sand, which chemically differs little in composition generally from its consolidated counterpart, a high SiO_2 content (say 95%) implies that most of that silica is free (quartz), little, if any, in combination. With total silica approaching 75%, Al_2O_3 , Na_2O , K_2O , and $\text{H}_2\text{O}+105^\circ\text{C}$. tend to increase proportionally according as aluminous silicates (e.g. kaolinite) or non-aluminous silicates (e.g. feldspar, ferromagnesian minerals) are present in the rock.

Exceptionally, sandstones cemented by or containing minerals other than silica, iron oxide, calcite, bitumen, etc., present interesting departures from straightforward silicate analysis, in that the invading media may bulk prominently in the result. Examples are fluorite (CaF_2) cement in Triassic Sandstone, Elgin, Scotland (up to 26%); malachite ($4(\text{Cu}_2\text{CO}_3(\text{OH})_2)$), barite (BaSO_4), and galena (PbS) in Keuper Waterstones (sandstone), Alderley Edge, Cheshire, where mineralization may be up to 15%; barite (BaSO_4) in other Triassic sandstones in Cheshire (up to 10%); witherite (BaCO_3) in Keuper Sandstone, Beeston Castle, Cheshire; gypsum (CaSO_4) in many desert sands: such abnormal cementing media are often occasioned by impregnating solutions of the salts concerned.

The old field-term 'greywacke' constantly occurs in literature and is still recognized in current specifications⁶. It is classified in the Arenaceous group (A2.6) and although technically a sandstone (see Vol. II, Ch. II), it represents a hybrid of every conceivable rock-type, according to locality: a problem, particularly in *interpretation* of analytical results, which at times can baffle the most

¹ F. W. Clarke, *The Data of Geochemistry*, U.S. Geol. Surv., Bull. 770, 1924, p. 30.

² *Principles of Geochemistry*, (John Wiley, New York), 1952, p. 130.

³ *Op. cit.*, p. 34.

⁴ *Op. cit.*, p. 547.

⁵ *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920.

⁶ See B.S. 812: 1960, p. 14.

experienced geochemist. Providing destabilization of mineral and rock fragments present in the sample under examination has not gone too far (which is rare), a microscopical examination may provide a solution, but even this technique is seldom convincing for these extremely variable and geologically ancient rocks. In short, at least from an academic standpoint, it is doubtful whether a chemical analysis of 'greywacke' is really worth while.

TABLE 7
ANALYSES OF SANDSTONE (A2.1)

CONSTITUENT	I	II	III	IV	V	VI	VII	VIII
SiO ₂	76.12	97.03	98.97	80.88	98.72	91.19	97.16	78.66
Al ₂ O ₃	10.93	1.61	0.46	9.80	0.65	4.94	0.22	4.78
Fe ₂ O ₃	3.03	0.38	0.02	2.36	0.10	0.51	0.82	1.08
FeO	0.23	—	—	—	—	0.14	—	0.30
MgO	1.63	0.11	0.07	0.31	0.01	0.07	0.04	1.17
CaO	0.39	0.02	0.10	0.20	tr.	0.05	0.18	5.52
Na ₂ O	2.41	0.15	nil	0.38	0.41	0.11	0.02	0.45
K ₂ O	1.87	0.14	0.08	1.13	0.14	1.51	0.11	1.32
H ₂ O+105°C.	2.04	0.35	—	2.60	0.24	1.21	0.30	1.33*†
H ₂ O-105°C.	0.82	0.03	—	0.68	0.04	0.17	0.02	0.31*
TiO ₂	0.67	0.07	0.04	0.65	0.17	0.20	1.24	0.25
P ₂ O ₅	0.14	0.02	—	0.03	nt. fd.	0.02	nt. fd.	0.08
MnO	0.01	0.18	—	0.12	nt. fd.	0.00	0.05	tr.
CO ₂	n.d.	0.02	—	0.85	nt. fd.	0.02	0.09	5.04
ZrO ₂	—	0.04	—	0.05	0.02	—	0.03	—
SO ₃	—	—	—	—	—	—	—	0.07
Cl	—	—	—	—	—	—	—	tr.
S	0.04	—	—	—	—	0.00	—	—
FeS ₂	—	nt. fd.	—	nt. fd.	nt. fd.	—	nt. fd.	—
Cr ₂ O ₃	0.01	—	—	—	—	—	—	—
NiO	}	nt. fd.	—	nt. fd.	nt. fd.	—	nt. fd.	—
CoO								
BaO								
SrO	tr.	—	—	—	—	0.06	—	0.05
Li ₂ O	—	—	—	—	—	—	—	nil
SrO	—	nt. fd.	—	nt. fd.	nt. fd.	—	nt. fd.	tr.
C	—	0.02	—	nt. fd.	nt. fd.	0.00	nt. fd.	—
Loss on Ignition	—	—	0.34	—	—	—	—	—
Totals (%)	100.34**	100.17	100.08	100.04	100.50	100.20,	100.28	100.41

* At 110°C.

† Includes organic matter.

** Add Spectrochemical determinations: SrO, —; Li₂O, 0.004; Rb₂O, 0.007; Cs₂O, n.d. < 0.02. *Anal.* C. O. Harvey, K. L. H. Murray.

- I Sandstone, Lealholm, Cleveland, Yorkshire (Inferior Oolite). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, p. 20. *Anal.* E. G. Radley.
- II Sandstone, Rishton Colliery, Rishton, near Blackburn, Lancashire (Coal Measures). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, p. 21. *Anal.* E. G. Radley.
- III Sandstone, Guisley Rock, Hawksworth Qy., Guisley, Yorkshire (Coal Measures). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, p. 16. *Anal.* E. G. Radley.
- IV Sandstone, Fallahill Qy., Fauldhouse, Linlithgowshire, Scotland (Coal Measures). *Sum. Prog. Geol. Surv. Gt. Brit.*, 1938, p. 94. *Anal.* G. A. Sergeant.
- V White Sandstone, Mold, Flintshire (Carboniferous Limestone). P. G. H. Boswell, *Brit. Res. Refractory Sands*, (Taylor and Francis, London), 1918, p. 103. *Anal.* H. F. Harwood and A. A. Eldridge.
- VI Sandstone, Mow Cop, Congleton Edge, Staffordshire (Lower Carboniferous, Pendleside). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, p. 221. *Anal.* E. G. Radley.
- VII Sandstone, Gartocharn, Dumbartonshire, Scotland (Lower Old Red Sandstone). *Sum. Prog. Geol. Surv. Gt. Brit.*, 1952, p. 48. *Anal.* R. Sawyer, P. Coombs.
- VIII Composite analysis of 253 sandstones. F. W. Clarke, *The Data of Geochemistry*, *U.S. Geol. Surv., Bull.* 770, 1924, p. 30. *Anal.* H. N. Stokes.

QUARTZITE (A2.4) AND GANISTER (A2.5).—Ganister is economically a significant variety of quartzite in Britain and because of certain distinctive petrographic characteristics, it is accorded recognition as a rock-type on its own merits (see Vol. II, Ch. II). Chemically, however, the two are normally indistinguishable, mineralogically pure types having a SiO_2 (free quartz) content from 97 to 98%. Of twenty-one British rocks designated quartzite, analysed as refractory materials by the Geological Survey, average SiO_2 content is 97%; of seven rocks designated specifically as ganister, analysed in that sense by the same authority, average SiO_2 content is 97%¹. With both types, decrease in silica purity is usually compensated by increase in alumina, alkalis and combined water; quartzites degenerate to sandstones, ganisters to silica rock or bastard ganister where SiO_2 content may be as low as 80%. It is perhaps noteworthy that on average quartzites and so-called ganisters of Scotland reveal less total SiO_2 than their English counterparts, being respectively 94.4% and 95%, as against 97% both in the latter categories².

¹ *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, pp. 15–26.

² *Op. cit.*, p. 34.

TABLE 8

ANALYSES OF QUARTZITE (A2.4) AND GANISTER (A2.5)

CONSTITUENT	I	II	III	IV	V	VI	VII	VIII
SiO ₂	97.02	97.99	99.26	98.85	97.70	96.87	93.69	61.20
Al ₂ O ₃	0.34	0.32	0.28	0.25	1.01	1.34	2.07	19.60
Fe ₂ O ₃	0.31	0.31	0.10	0.31	0.47	0.44	0.87	1.27
FeO	—	—	—	—	—	—	—	4.50
MgO	0.13	0.17	0.01	0.02	0.05	0.09	0.09	2.42
CaO	0.05	0.04	0.02	0.04	0.06	0.08	1.26	1.23
Na ₂ O	0.17	0.21	0.34	0.13	0.03	0.24	0.45	0.45
K ₂ O	0.09	0.09	0.08	0.07	0.20	0.72	1.38	3.62
H ₂ O + 105°C.	0.42	0.30	0.09	0.17	0.36	0.19	0.15	3.81
H ₂ O - 105°C.	0.02	0.04	0.04	0.05	0.13	0.06	0.01	0.14
TiO ₂	0.22	0.42	0.13	0.03	0.10	0.03	0.08	0.34
P ₂ O ₅	0.02	0.02	nt. fd.	nt. fd.	0.03	0.01	nt. fd.	0.07
MnO	0.10	0.09	nt. fd.	0.02	0.02	0.04	0.04	0.09
CO ₂	0.04	0.03	nt. fd.	0.06	0.03	0.04	0.08	0.58
ZrO ₂	0.18	0.15	0.02	0.05	0.05	0.04	0.03	—
SO ₃	—	—	—	—	—	—	—	0.05
F	—	—	—	—	—	—	—	n.d.
S	—	—	—	—	—	—	—	0.37
FeS ₂	0.49	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	0.06	—
Cr ₂ O ₃	—	—	—	—	—	—	—	0.10
NiO } CoO }	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	—
BaO }	—	—	—	—	—	—	—	0.05
Li ₂ O	nt. fd.	nt. fd.	nt. fd.	nt. fd.	tr.	nt. fd.	nt. fd.	—
C	0.44	0.04	nt. fd.	0.01	tr.	tr.	tr.	—
Totals (%)	100.04	100.02	100.37	100.06	100.24	100.19	100.26	99.89*

* Less O for S: 0.19. Total 99.70%.

- I Ganister, Oughtibridge, Yorkshire (Coal Measures). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, p. 16. *Anal.* E. G. Radley.
- II Ganister, Morredge Mine, Totley, Derbyshire (Coal Measures). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, p. 20. *Anal.* E. G. Radley.
- III Quartzite, Guiseley, Yorkshire (Millstone Grit). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, p. 19. *Anal.* E. G. Radley.
- IV Quartzite, Craig-y-nos (Penwyllt), Brecknockshire (Millstone Grit). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, p. 22. *Anal.*, E. G. Radley.
- V Quartzite, Bwlchgwyn, Minera, Denbighshire (Millstone Grit). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, p. 22. *Anal.* E. G. Radley.
- VI Quartzite, Hartshill, Nuneaton, Warwickshire (Cambrian). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, p. 21. *Anal.* E. G. Radley.

- VII Quartzite, Lagenha, Kentallen, Argyllshire (Pre-Cambrian). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, p. 25. *Anal.* E. G. Radley.
- VIII Quartzite (Banket groundmass), Witwatersrand, S. Africa. *Med. Res. Council, Chronic Pulmonary Disease in S. Wales Coalminers, II. Environmental Studies, Spec. Rep. Series 244*, 1943, p. 146. *Anal.* Geochemical Laboratories.

CLAY (A3.1) AND FIRECLAY (A3.2).—With the enormous growth within the last two decades of our knowledge of clay as substance, as rock geologically considered, in the science of clay mineralogy and in its own technology, due in no small measure to intensive X-ray studies of the crystal structure of clay minerals *per se*, it is not surprising to find that authoritative published chemical analyses of clays, particularly of clay minerals, far outweigh those available today of arenaceous or calcareous sedimentary rocks. To this extent, chemical analyses of clay as rock, if not interpreted in terms of actual clay-mineral composition, would appear to have strictly limited academic, but not necessarily industrial value. Regarded from the former viewpoint we can only agree with R. E. Grim: 'The analysis of a clay material must be tailor-made to the material being studied and to the purpose of the investigation and must provide comparable results from one sample to another. One cannot blindly use a set analytical procedure for all materials and all problems and still get adequate data without a tremendous waste of time and effort'¹. From a commercial angle, in ceramic and all related industries where clay of one sort or another is fundamental raw material, ultimate chemical analyses of clay samples are still sought, if only as comparative or sorting tests.

The specialized subject of clay minerals is ably dealt with in general principles by D. Carroll in this book (Vol. II, Ch. III), to which the reader is directed for current information and literature. In this section data are confined to analyses of certain well-known British clays and fireclays; also to analyses of some of the more important clay minerals. Many chemical analyses of British fireclays are contained in a Geological Survey publication (which also includes valuable discussion of chemical and physical tests involved in their investigation) to which the reader is accordingly referred². For full description of clay minerals and chemical analyses, the works of R. E. Grim³ and G. W. Brindley⁴ should be consulted.

¹ *Clay Mineralogy*, (McGraw-Hill, New York), 1953, p. 5.

² *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XXVIII, 1924.

³ *Op. cit.*

⁴ *X-Ray Identification and Crystal Structures of Clay Minerals*, (*Min. Soc.*, London), 1951.

TABLE 9

ANALYSES OF CLAY (A3.1) AND FIRECLAY (A3.2)

CONSTITUENT	I	II	III	IV	V	VI	VII	VIII
SiO ₂	59.61	53.26	39.44	60.93	66.38	60.29	69.67	65.06
Al ₂ O ₃	26.11	17.05	15.88	18.02	12.55	16.73	18.21	20.05
Fe ₂ O ₃	1.06	4.72	4.26	3.15	2.20	2.02	0.76	0.38
FeO	—	2.02	0.91	2.99	0.92	1.92	0.64	2.12
MgO	0.23	3.39	1.61	1.10	0.93	1.48	0.64	0.94
CaO	0.30	1.60	13.90	0.67	1.95	0.65	0.53	0.62
Na ₂ O	0.25	0.30	0.36	0.40	0.51	0.87	0.19	0.76
K ₂ O	2.52	3.20	2.59	2.21	2.25	2.75	0.86	2.75
H ₂ O + 105°C.	7.11	5.35	5.31	5.73	3.78	4.29	5.86	3.01
H ₂ O - 105°C.	1.36	5.26	3.98	2.58	3.22	2.61	1.58	1.04
TiO ₂	1.36	0.95	0.71	1.17	0.78	0.92	1.06	0.88
P ₂ O ₅	0.07	0.14	0.03	0.07	0.07	0.06	0.05	0.11
MnO	0.01	0.03	0.04	0.07	0.01	0.03	0.04	tr.
CO ₂	—	1.40	10.66	0.20	0.68	0.37	0.07	0.63
ZrO ₂	0.03	—	—	—	—	—	0.02	—
SO ₃	tr.	0.23	0.08	0.00	0.98	0.57	0.04	—
Cl	—	—	—	—	—	—	0.04	—
F	0.03	—	—	—	—	—	—	tr.
S	tr.	—	—	—	—	—	—	0.08
FeS ₂	—	0.43	0.00	0.54	1.88	3.04	0.04	—
Fe ₇ S ₈	—	—	—	—	0.00	0.00	—	—
Cr ₂ O ₃	0.01	0.02	0.01	0.01	0.01	0.01	—	—
V ₂ O ₅	0.02	—	—	—	—	—	—	—
NiO	—	—	—	—	—	—	0.01	—
BaO	0.04	0.02	0.02	0.04	0.03	0.03	tr.	nil
SrO	—	—	—	—	—	—	nil	—
Li ₂ O	tr.	—	0.06	—	—	—	0.05	—
C	tr.	0.33	0.40	0.50	0.62	1.06	0.12	1.82
Carb. matter	0.29	—	—	—	—	—	—	—
Org. H	—	—	—	—	—	—	0.04	—
Totals (%)	100.41	99.70	100.25	100.38	99.75	99.70	100.53	100.25*

* Less O for S: 0.04%. Total 100.21%.

- I Pipe-clay, Bovey Basin, S. Devon (Miocene). A. Scott, *Ball Clays*, *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XXXI, 1929, p. 45.
- II London Clay, Worcester Park, Surrey (Eocene). *Sum. Prog. Geol. Surv. Gt. Brit.*, 1935 (1936), p. 93. *Anal. C. O. Harvey.*
- III Gault Clay, Cottenham, Cambridgeshire (Upper Cretaceous). *Sum. Prog. Geol. Surv. Gt. Brit.*, 1935 (1936), p. 94. *Anal. C. O. Harvey.*
- IV Weald Clay, North Holmwood, Surrey (Lower Cretaceous). *Sum. Prog. Geol. Surv. Gt. Brit.*, 1935 (1936), p. 94. *Anal. C. O. Harvey.*
- V Kimmeridge Clay, Swindon, Wiltshire (Jurassic). *Sum. Prog. Geol. Surv. Gt. Brit.*, 1935 (1936), p. 94. *Anal. C. O. Harvey.*
- VI Oxford Clay, Chickerell, Weymouth, Dorset (Jurassic). *Sum. Prog. Geol. Surv. Gt. Brit.*, 1935 (1936), p. 94. *Anal. C. O. Harvey.*

- VII Fireclay, Wilnecote, Warwickshire (Coal Measures). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XXVIII, 1924, p. 32. *Anal.* Government Chemist.
- VIII Fireclay (Stanlyd Seam), Coal Measures, S. Wales. Medical Research Council, Chronic Pulmonary Disease in S. Wales Coalminers, *Spec. Rep.* 244, 1943, p. 146. *Anal.* W. H. Herdsman.

TABLE 10

ANALYSES OF CLAY MINERALS

CONSTITUENT	I	II	III	IV	V	VI	VII	VIII
SiO ₂	47.55	52.70	51.14	46.77	44.46	46.86	36.13	46.54
Al ₂ O ₃	32.45	14.84	19.76	37.79	36.58	37.12	13.90	36.37
Fe ₂ O ₃	0.76	4.91	0.83	0.45	0.36	1.43	4.24	0.72
FeO	1.85	0.98	—	0.11	0.07	0.06	0.68	0.36
MgO	1.70	3.60	3.22	0.24	0.18	0.09	24.84	0.50
CaO	0.06	2.72	1.62	0.13	0.19	0.22	0.18	0.22
Na ₂ O	1.05	nil	0.04	0.05	0.01	0.07	—	0.46
K ₂ O	6.22	nil	0.11	1.49	0.51	0.60	—	8.06
H ₂ O+105°C.	7.73	} 20.0	7.99	12.18	13.38	12.77	} 18.94	6.31
H ₂ O-105°C.	—		14.81	0.61	4.05	0.29		0.52
TiO ₂	0.64	—	—	—	0.15	0.51	0.24	0.17
P ₂ O ₅	—	—	—	—	—	—	—	0.06
MnO	—	—	—	—	—	—	tr.	nil
F	—	—	—	—	—	—	—	0.02
NiO	—	—	—	—	—	—	0.28	—
Totals %	100.01	99.77	99.52	99.82	99.94	100.02	99.43	100.31*

* Less O for F: 0.01 %. Total 100.30 %.

- I Illite, average analysis at 105°C. D. Hicks and G. Nagelschmidt, Med. Res. Council, Chronic Pulmonary Disease in S. Wales Coalminers, *Spec. Rep.* 244, 1943, p. 164.
- II Montmorillonite, average 4 analyses, Fuller's Earth, Nutfield, Surrey. A. Brammall and J. G. C. Leech, *Geol. Mag.*, 77, 1940, p. 109.
- III Montmorillonite, Montmorillon, France. R. E. Grim, *Clay Mineralogy*, (McGraw-Hill, New York), 1953, p. 371. *Anal.* quoted from C. S. Ross and S. B. Hendricks, *U.S.G.S., Prof. Paper* 205B, 1945.
- IV Kaolinite, St. Austell, Cornwall. R. E. Grim, *op. cit.*, p. 370. *Anal.* quoted from P. F. Kerr *et al.*, *Rep. 7, Amer. Pet. Inst.*, Project 49, 1950.
- V Halloysite, Bedford, Indiana, U.S.A. R. E. Grim, *op. cit.*, p. 370. *Anal.* quoted from P. F. Kerr *et al.*, *Rep. 7, A.P.I. Project* 49, 1950.
- VI Dickite, Anglesey, Wales. R. E. Grim, *op. cit.*, p. 370. *Anal.* quoted from P. F. Kerr *et al.*, *Rep. 7, A.P.I. Project* 49, 1950.
- VII Vermiculite, Bare Hills, Baltimore, Maryland, U.S.A. G. W. Brindley and *ors.*, *X-ray Identification and Crystal Structures of Clay Minerals*, (Mineralogical Society, London), 1951, p. 221. *Anal.* quoted from J. W. Gruner, *Amer. Min.*, 19, 1934, pp. 557-575.

VIII Hydromuscovite (Sericite), Ogfa, Carmarthenshire, Wales. A. Brammall, J. G. C. Leech and F. A. Bannister, *Miner. Mag.*, 24, 1937, p. 507.

Anal. Miss H. Bennett.

FULLER'S EARTH (A3.3), MUDSTONE (A3.8) AND SHALE (A3.9).—Of these argillaceous types, Fuller's Earth is lithologically the most interesting on account of peculiar, inherent physical properties, intimately bound up with its chief constituent montmorillonite (approx. formula $4\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot (1+x)\text{H}_2\text{O}$), a hydrated aluminosilicate containing lime, magnesia and iron (Table 10), sometimes alkalis, with essential properties of high base-exchange

TABLE 11
ANALYSES OF FULLER'S EARTH (A3.3),
MUDSTONE (A3.8), AND SHALE (A3.9)

CONSTITUENT	I	II	III	IV	V	VI	VII	VIII
SiO ₂	56.89	58.45	56.65	59.37	50.75	46.99	55.02	58.38
Al ₂ O ₃	15.11	15.45	19.70	19.61	18.75	25.34	21.02	15.47
Fe ₂ O ₃	5.80	8.65	4.05	0.84	2.80	2.33	5.00	4.03
FeO	0.83	0.90	0.40	5.42	—		1.54	2.46
MgO	3.13	3.00	2.10	2.26	0.80	1.42	2.32	2.45
CaO	4.27	2.40	4.75	0.57	0.29	0.34	1.60	3.12
Na ₂ O	0.30	0.30	0.70	1.18	0.14	0.66	0.81	1.31
K ₂ O	0.74	0.70	1.80	3.12	1.49	3.79	3.19	3.25
H ₂ O+105°C.	6.23	—	—	5.03	—	6.19	5.65	5.02
H ₂ O-105°C.	4.79	—	—	1.18	—	1.39	2.44	
TiO ₂	0.66	—	—	0.98	0.99	0.63	0.65	0.65
P ₂ O ₅	0.10	—	—	0.16	0.02	0.11	0.06	0.17
MnO	0.01	—	—	0.13	0.01	0.28	tr.	tr.
CO ₂	1.20	—	1.85	0.03	—	2.89	0.83	2.64
SO ₃	—	—	—	—	0.00	nil	0.02	0.65
F	0.08	—	—	<0.00	—	n.d.	—	—
S	—	—	—	—	—	0.20	—	—
BaO	0.12	—	—	—	0.03	0.07	0.04	0.05
SrO	—	—	—	—	—	—	—	nil
Li ₂ O	—	—	—	—	tr.	—	0.03	tr.
C	—	—	—	0.20	—	—	0.32	0.81
Loss on Ignition	—	10.15	7.90	—	24.00	—	—	—
Totals (%)	100.26	100.00	99.90	100.08	100.07†	92.63*	100.54	100.46

* Less O for S: 0.10%. Total 92.53%.

† H₂O+105°C., 1.55%; H₂O-105°C., 1.55%; CO₂, 0.35%; S, 0.20%; C, 12.82%.

- I Fuller's Earth, Nutfield, Surrey. A. Brammall and J. G. C. Leech, *Geol. Mag.*, 77, 1940, p. 104. *Anal. Geochemical Laboratories.*
- II Fuller's Earth, Woburn, Bedfordshire. Jurassic Rocks of Britain, *Mem. Geol. Surv.*, 4, 1894, p. 491. (Average 2 analyses, blue and yellow earths).
- III Fuller's Earth, Midford, Somerset. Jurassic Rocks of Britain, *Mem. Geol. Surv.*, 4, 1894, p. 491 (Average 2 analyses, blue and yellow earths).
- IV Mudstone ('Accrington Shale'), Accrington, Lancashire (Lower Coal Measures). *Anal. Geochemical Laboratories.*
- V Mudstone ('Blaes'), Tullibody B.H.2, Cambus, Clackmannan, Scotland (Carboniferous Limestone). *Sum. Prog. Geol. Surv. Gt. Brit.*, 1938, p. 95. *Anal. G. A. Sergeant.*
- VI Shale ('Clod'), S. Wales Coalfield (Coal Measures). Medical Research Council, Chronic Pulmonary Disease in S. Wales Coalminers. *Spec. Rep.* 244, 1943, p. 146. *Anal. Geochemical Laboratories.*
- VII Shale, Coosa Valley, Alabama, U.S.A. (Middle Cambrian). Quoted by F. W. Clarke (ref. No. VIII below, p. 552). *Anal. H. N. Stokes.*
- VIII Shale, composite analysis of 78 samples. F. W. Clarke The Data of Geochemistry, *U.S.G.S., Bull.* 770, 1924, p. 631.

capacity and marked reversible lattice-shrinkage on dehydration¹. Incidentally this is the operative mineral in the rock bentonite (Vol. II, Ch. II). renowned for its remarkable swelling properties.

In the Lower Greensand Fuller's Earth (Nutfield, Surrey), when the clay fraction is segregated, montmorillonite makes up 76–90% of that fraction². R. E. Grim³ quotes seven chemical analyses of this mineral from different world sources; their average composition works out at SiO₂, 52.36%; Al₂O₃, 18.30%; Fe₂O₃, 2.58%; MgO, 3.93%; CaO, 13.07%; K₂O (on six samples), 0.36%; Na₂O (on six samples), 0.77%; hygroscopic water (on four samples), 15.22%; combined water (on five samples), 7.85%. The Si:Al ratio may vary in different montmorillonites from 1:1 to 3:1. For a full academic discussion of montmorillonite minerals (montmorillonoids) the reader should consult reference⁴ below.

In mudstone (A3.8) we recognize a type representing first phase consolidation of clay-sediment, the non-laminated phase. In shale (A3.9) compaction has gone a stage further towards lamination and crystallization. From both mineralogical and chemical angles, this dead-weight pressure on clay substance is a far-reaching mechanism and is frequently reflected in appropriate chemical analyses.

¹ M. H. Hey, *Index of Mineral Species and Varieties*, (British Museum, London), 1950, p. 144 and refs. cited.

² A. Brammall and J. G. C. Leech, *Geol. Mag.*, 77, 1940, p. 103.

³ *Clay Mineralogy*, (McGraw-Hill, New York), 1953, p. 371.

⁴ D. M. C. MacEwan, *X-ray Identification and Crystal Structures of Clay Minerals* (Mineralogical Society, London), 1951, Ch. IV. See also D. Carroll, Vol. II, Ch. III.

'Compaction tends to reduce the quantity of indeterminate mineral matter, by progressively aggrading it to more definitely crystalline and specific minerals this reconstitution-and-recrystallization process may be said to involve a reversal of the effects of 'weathering'. Whereas weathering is characterized by the breakdown of crystal structure, to the accompaniment of hydration, oxidation, a variable degree of de-silication, and the leaching of the more mobile bases—typically as carbonates—metamorphism due to compaction is characterized by dehydration, de-oxidation (*e.g.* the reduction of ferric to ferrous oxide), and decarbonatization, accompanied by re-silication and the 'fixing' of mobile bases in definitely specific crystalline compounds. Clay colloids undergo progressive dehydration; adsorbed bases enter mica, chlorite, feldspar, etc.; alumina and silica adjust themselves to proportions proper to such specific minerals evolving under physical conditions which are themselves changing; ferric oxide tends to be reduced to ferrous oxide and to enter new minerals, and even carbonates may be destabilized—in favour of silicates'¹.

The sequence clay-shale-slate-schist, postulates at least in the two latter rock-types, transition from sedimentary to metamorphic rock, since 'Slates originate from shales under intense lateral compression, whereby shale mineralogy is aggraded and simplified to (a) a metastable ternary system composed of quartz, sericite-mica, and chlorite, associated with (b) subordinate amounts of minor accessory species—typically rutile, carbonate, pyrite, and epidote, with some others of more casual occurrence There is little, if any, amorphous residuum'².

In this sequence of events, there would appear to be established through clay, shale, slate to schist end point, a fundamental trend to progressive *increase* in SiO_2 , Al_2O_3 , FeO , $\text{Na}_2\text{O} + \text{K}_2\text{O}$, and *decrease* in Fe_2O_3 , $\text{CaO} + \text{MgO}$, H_2O , and CO_2 ; this is attested by average of 12 analyses (clays and soils); composite analysis of 78 shales (Table 11, VIII); average of 22 analyses of slates; and of 5 analyses of schists, given by F. W. Clarke³. The mechanism implied in this deduction invites more intensive geochemical investigation than has yet been accorded it, either by chemists or mineralogists.

MARL, MARLSTONE (AB.1) AND CALCAREOUS SHALE (AB.2).—This group is in many respects unsatisfactory. As with igneous rocks, certain hybrid types (*e.g.* granophyre-gabbro complex, Carrock Fell, Cumberland) defy systematic classification, so it happens with sediments. Transitional facies between strictly detrital on the one hand and essentially organic rock-types on the other, are

¹ A. Brammall and J. G. C. Leech, Chronic Pulmonary Disease in South Wales Coalminers, II. Environmental Studies. E—The Petrology of Coal Measures, Shales and Sandstones. Privy Council, *Spec. Rep.*, Series 244, (H.M.S.O., London), 1943, pp. 127–128.

² A. Brammall and J. G. C. Leech, *op. cit.*, p. 128.

³ The Data of Geochemistry, *U.S.G.S. Bull.* 770, 1924, p. 631.

TABLE 12

ANALYSES OF MARL (AB.1), MARLSTONE (AB.1),
AND CALCAREOUS SHALE (AB.2)

CONSTITUENT	I	II	III	IV	V	VI	VII
Insol.	14.30	6.09	—	—	—	—	—
SiO ₂	2.13	16.71	5.1	38.00	17.00	13.33	25.05
Al ₂ O ₃	0.10	—	5.2	14.85	5.99	4.76	8.28
Fe ₂ O ₃	} 1.97	} 0.78	22.0	4.75	4.16	2.87	0.27
FeO							
MgO	0.74	0.83	0.7	3.42	1.18	15.35	2.61
CaO	45.34	40.76	33.0	17.78	36.10	23.98	27.87
Na ₂ O	} 1.68	tr.	—	—	—	0.12	—
K ₂ O		tr.	—	—	—	1.33	—
H ₂ O+105°C.	—	—	2.1	—	—	—	2.86
H ₂ O-105°C.	—	—	—	—	—	1.03	1.44
TiO ₂	—	—	0.2	—	—	0.22	—
P ₂ O ₅	0.13	0.24	0.6	—	—	0.10	0.08
MnO	—	—	0.2	—	—	0.19	4.11
CO ₂	33.34	33.05	—	—	—	34.01	28.20
SO ₃	0.14	1.55	—	1.28	0.59	—	—
S	—	—	0.1	—	—	—	—
FeS ₂	—	—	—	—	—	0.48	—
Cr ₂ O ₃	—	—	tr.	—	—	—	—
V ₂ O ₃	—	—	tr.	—	—	—	—
Loss on Ignition	—	—	30.7	19.92	34.98	2.14	—
Totals (%)	99.87	100.01†	99.9†	100.00	100.00	99.91*	99.18

† In analysis II above, probable combinations are SiO₂ (clay and quartz) 22.8%; CaCO₃, 70.35%; MgCO₃, 1.73%; CaSO₄, 2.62%.

‡ Total Fe content 15.4%.

* In analysis VI above, total insoluble residue is 21.40%; CaCO₃, 42.80%; MgCO₃, 32.10%.

- I Chalk Marl, Farnham, Surrey (Upper Cretaceous). A. J. Jukes-Browne, *The Cretaceous Rocks of Britain*, II, *Mem. Geol. Surv.*, 1903, p. 333. Average 2 analyses.
- II Chalk Marl, Wiltshire (Upper Cretaceous). A. J. Jukes-Browne, *op. cit.*, p. 334. *Anal.* Voelcker.
- III Marlstone, Bloxham, Oxfordshire (Liassic). The Liassic Ironstones, *Mem. Geol. Surv. Gt. Brit.*, 1952, p. 201. *Anal.* G. A. Sergeant.
- IV Calcareous Shale, Warwickshire (Lias). F. M. Lea, *The Chemistry of Cement and Concrete*, 2nd ed. (Arnold, London), 1956, p. 24.
- V Calcareous Shale, Warwickshire (Lias). F. M. Lea, *op. cit.*, p. 24.
- VI Calcareous or Marly Shale, Ballagan Burn, Strathblane, Stirlingshire (Carboniferous). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XXXV, 1949, p. 178. *Anal.* A. Muir and A. G. M. Hardie.
- VII Calcareous Shale, Mount Diablo, California, U.S.A. (Cretaceous). F. W. Clarke, *The Data of Geochemistry, U.S.G.S. Bull.* 770, 1924, p. 552. *Anal.* W. H. Melville.

widely developed everywhere and for that reason alone merit detached consideration. But economically both marl and marlstone are of importance in their contribution, as raw materials, to manufacture of cement and steel.

Interpreting the term marl to mean calcareous clay (Vol. II, Ch. II), every lithological gradation between calcareous mud (e.g. ooze, B1.4), consolidated marl (e.g. Keuper and Chalk Marls), laminated marl (e.g. in Keuper Waterstones), to marlstone 'rock-bed' (e.g. Liassic bedded iron ore) can be found in the stratigraphical sequence. Shales which have undergone infusion of lime, probably during their mudstone phase (p. 340), are designated 'calcareous' because of their usually prominent carbonate content; they have close affinities with laminated marls. Petrologically, these sedimentary rock-types sometimes present difficulties in complete mineralogical interpretation and it is on these occasions that their chemical analyses, if and when available, do much to assist diagnosis.

As would be anticipated from the nature of these rocks, chemical records reveal that they are subject to great variation in composition. There tends to be a reciprocal relationship between $\text{SiO}_2 + \text{Al}_2\text{O}_3$ on the one hand, and $\text{CaO} + \text{MgO}$ on the other. F. M. Lea¹ quotes data from the famous Lehigh district of Pennsylvania, U.S.A., where so-called 'cement rock' consists of argillaceous limestone (including calcareous shale); average composition: SiO_2 , 16–21%; Al_2O_3 , 4–8%; Fe_2O_3 , 1–2%; CaO , 35–41%; MgO , 2%. Again, the Ballagan Beds near Strathblane, Stirlingshire (Carboniferous), provide another illustration of the same tendency²: $\text{SiO}_2 + \text{Al}_2\text{O}_3$, 18.09%; $\text{CaO} + \text{MgO}$, 39.33% (Table 12) for a marl which, at the same place and in the same sequence, degenerates into a calcareous or marly shale having $\text{SiO}_2 + \text{Al}_2\text{O}_3$, 61.30% and $\text{CaO} + \text{MgO}$, 12.9%. In 6 analyses of the well-known Chalk Marl from Cherry Hinton, Cambridgeshire, ratios of insoluble siliceous matter to CaCO_3 were respectively 47.2%: 49.0%; 24.6%:65.7%; 16.2%:70.5%; 21.3%:76.2%; 20.1%: 76.5%; 26.2%:70.0%. An interesting point in this series is that those ratios represent samples taken progressively from 5 ft. to 23 ft. below surface in the quarry concerned³.

The analyses quoted in Table 12 above have been selected as a

¹ *The Chemistry of Cement and Concrete*, 2nd ed., (Arnold, London), 1956, p. 24.

² T. Robertson, J. B. Simpson and J. G. C. Anderson, *The Limestones of Scotland*, *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XXXV, 1949, pp. 177–178.

³ A. J. Jukes-Browne, *The Cretaceous Rocks of Britain*, II, *Mem. Geol. Surv.*, 1903, p. 335. *Anal. J. W. Knights*.

guide to what to expect when these sediments are chemically examined. It should be noted that a further example of marlstone analysis is given under Ferruginous Deposits (p. 363).

LIMESTONE (B1.1), DOLOMITIC LIMESTONE (B1.2), AND CHALK (B1.5).—Pure calcium carbonate CaCO_3 (calcite) contains 56.03% CaO and 43.97% CO_2 ; hence the closer a calcareous rock approaches those proportions, the purer is likely to be the limestone, chalk, calcareous mud, ooze or whatever other type is involved. It is, however, unusual to find a limestone (even chalk) absolutely pure; an approach to this is made by the well-known Ribblesdale White Limestone, Horton Quarries, Settle, Yorkshire (Carboniferous), where $\text{CaO} : \text{CO}_2$ is 55.50% : 43.80%, with only 0.61% impurity¹. In the case of a composite analysis of 345 limestones quoted by F. W. Clarke² (see Table 13), figures for CaO and CO_2 were 42.61% and 41.58% respectively. The purest chalk in England contains 97–98% CaCO_3 , the balance usually being SiO_2 , other detrital matter, iron and, sometimes, traces of MgCO_3 .

More often than not nowadays, chemical analyses of limestones, dolomites too for that matter, especially for industrial purposes, express composition in terms of calcium and/or magnesium carbonate, not as oxides. Where, however, nature and amounts of impurities are of importance, fuller conventional analyses are inevitable, whence conversion to essential minerals and accessories is seldom difficult unless lime and/or magnesia are present in some other form, *e.g.* calc-silicates, which means silicate analysis. In straightforward cases factors for CaCO_3 are $\text{CaO} \times 1.784$ and for MgCO_3 , $\text{MgO} \times 2.091^3$.

In dolomitic limestone (dolomite), if pure, the ratio is CaCO_3 54.35% : MgCO_3 45.65%, which in terms of $\text{CaO} : \text{MgO}$ is 1 : 1.4. Of a total of 29 British Carboniferous dolomites analysed by the Geological Survey⁴, the ratio of CaCO_3 to MgCO_3 is 54.57% : 39.45%; of a total of 16 British Permian dolomites analysed by the same authority, ratio of CaCO_3 to MgCO_3 is 54.21% : 41.57%; thus chemically it appears to indicate, as is often evident in the field by their lithological characteristics, that in Britain Permian tend to be purer than Carboniferous dolomites. As regards minor constituents in these rocks, iron may either be present as siderite (FeCO_3) or limonite (hydrated oxide of iron);

¹ J. Watson, *British and Foreign Building Stones*, (University Press, Cambridge), 1911, p. 269.

² The Data of Geochemistry, *U.S.G.S. Bull.* 770, 1924, p. 564.

³ T. Robertson, J. P. Simpson and J. G. C. Anderson, The Limestones of Scotland, *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XXXV, 1949, p. 29.

⁴ H. H. Thomas, A. F. Hallimond and E. G. Radley, *Refractory Materials*, etc., *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, Ch. IX.

manganese usually denotes rhodochrosite (MnCO_3); gypsum (CaSO_4) is not an infrequent occurrence; alumina commonly represents clay-substance in which combined silica is involved; some dolomites exhibit free silica (quartz): this is often of secondary origin.

Chalk, as previously stated, ranges from 97 to 98% CaCO_3 in its purest form. From a survey carried out by the author in the Marlborough region, Wiltshire, of Middle Chalk potential to agricultural lime (minimum requirements 90% CaCO_3), 11 samples analysed averaged 94.24% CaCO_3 ¹. Average analyses of Kentish white and grey chalk used for cement manufacture are 98.25% and 90.55% CaCO_3 respectively². The famous red chalk of Hunstanton, Norfolk, contains 74% CaCO_3 , 1.93% MgCO_3 , 4.62% Fe_2O_3 and 9.18% SiO_2 , a rock in a class by itself³.

It has been shown⁴ that silica tends to be less abundant in Upper Chalk, normally prolific in flint content, than Lower Chalk in which flint is altogether wanting. There is traceable a gradual increase in silica content with downward succession (stratigraphically) of chalk strata.

G. E. Bessey and D. C. Soul have discussed the probable form of essential constituents found by analyses of chalks used for whiting, as follows⁵:

CONSTITUENT		COMPOSITION OF CHALK	
		<i>Probable range</i>	<i>Probable form</i>
Silica	SiO_2	Up to 5%	Probably present as quartz, flint and silicates.
Iron Oxide	Fe_2O_3	Up to 0.20%	Probably present as clay minerals, ferrous carbonate or free hydrated oxides.
Aluminium Oxide	Al_2O_3	Up to 1.0%	
Magnesium Oxide	MgO	Up to 0.8%	Present mainly as carbonates.
Calcium Oxide	CaO	50–56%	Present mainly as carbonates.
Manganese	Mn	Up to 0.07%	Present mainly as carbonates.
Copper	Cu	Up to 0.004%	Present mainly as carbonates.
Sulphate	SO_3	Up to 1.0%	Probably present as calcium, magnesium, or alkali salts.
Carbonate	CO_2	38–44%	
Phosphate	P_2O_5	Up to 0.10%	
Acid insoluble matter		1 in to 6%	Includes siliceous matter and detrital minerals.

¹ Geochemical Laboratories, 1951.

² F. M. Lea, *The Chemistry of Cement and Concrete*, 2nd ed., (Arnold, London), 1956, p. 23.

³ J. Watson, *op. cit.*, p. 317.

⁴ W. A. Richardson, The Origin of Cretaceous Flint, *Geol. Mag.*, **56**, 1919, pp. 535–547.

⁵ The Chemical Analysis of Whiting and Chalk, Research Council Brit. Whiting Fed., *Tech. Paper 4*, 1950, p. 2.

'In addition to these constituents, which account in nearly all whittings for over 99% of the sample, there may be present some combined water, particularly associated with the clayey matter, alkalis (soda or potash), organic matter, and possibly traces of a number of other elements. None of these are however at present known to be of practical importance'¹

TABLE 13
ANALYSES OF LIMESTONE (B1.1) AND
DOLOMITIC LIMESTONE (B1.2)

CONSTITUENT	I	II	III	IV	V	VI	VII	VIII
Insol. Res.	—	—	3.23	—	—	—	0.44	4.09
SiO ₂	0.42	0.93	0.32	1.60	19.60	5.19	0.21	0.23
Al ₂ O ₃	0.46	0.31	0.20	0.10	4.00	0.81	0.02	1.30
Fe ₂ O ₃	} 1.22	0.72	0.04	} 0.27	0.09	0.54	1.73	0.13
FeO			0.13		1.02	—	0.22	0.59
MgO	0.32	0.32	0.60	0.68	1.81	7.90	20.46	18.83
CaO	53.55	53.65	52.97	54.60	38.68	42.61	30.35	29.75
Na ₂ O	0.44	0.38	—	—	0.55	0.05	—	—
K ₂ O	—	—	—	—	0.87	0.33	—	—
H ₂ O+105°C.	} 0.88	0.74	0.32	—	0.96	0.56	0.36	0.51
H ₂ O-105°C.			0.31	—	0.30	0.21	0.02	0.12
TiO ₂	—	—	—	—	0.24	0.06	—	—
P ₂ O ₅	—	—	0.04	tr.	0.10	0.04	—	—
MnO	—	—	0.04	—	0.08	0.05	0.03	0.05
CO ₂	42.04	42.26	41.98	42.70	31.30	41.58	46.08	44.19
SO ₃	tr.	0.11	0.03	0.03	nd.	0.05	0.41	0.32
Cl	0.03	—	—	—	—	0.02	—	—
S	—	—	—	—	—	0.09	—	—
FeS ₂	—	—	—	—	0.75	—	nt. fd.	—
Cr ₂ O ₃	—	—	—	—	tr.	—	—	—
BaO	—	—	—	—	tr.	—	—	—
SrO	—	—	—	—	0.10*	—	—	—
Li ₂ O	—	—	—	—	—	tr.	—	—
C	—	—	0.06	—	—	—	0.01	0.14
Totals (%)	99.36	99.42	100.27	99.98	100.45	100.09	100.34	100.25

* Determined spectrochemically by C. O. Harvey and K. L. H. Murray.

- I Limestone (Bath Stone), Bath, Somerset (Great Oolite). T. Ransome and B. Cooper, *Mem. Geol. Surv.*, I, 1848, pp. 685-702.
- II Oolitic Limestone, Dundry, Somersetshire (Inferior Oolite, Jurassic). T. Ransome and B. Cooper, *Mem. Geol. Surv.*, II, 1848, pp. 685-702. *Anal. Prof. Daniell.*
- III Limestone (Whitehead Limestone), Symonds Yat, Herefordshire (Carboniferous Limestone). *Sum. Prog. Geol. Surv. Gt. Brit.*, 1936, p. 86. *Anal. C. O. Harvey.*

¹ See ref. 5, p. 345.

- IV Limestone, Trefil, Tredegar, Monmouthshire (Carboniferous Limestone). T. Robertson, *Mem. Geol. Surv.*, 232, 2nd ed., 1927, p. 128. *Anal.* Ebbw Vale Steel, Iron and Coal Co. Ltd.
- V Limestone, Pennyhill Qy., Martley, Worcestershire (Wenlock). *Sum. Prog. Geol. Surv., Gt. Brit.*, 1952, p. 48. *Anal.* R. Sawyer and P. Coombs.
- VI Limestone. Composite analysis 345 limestones, by H. N. Stokes. Quoted by F. W. Clarke, *The Data of Geochemistry, U.S.G.S. Bull.* 770, 1924, p. 564.
- VII Dolomite, Hampole, near Doncaster, Yorkshire (Permian). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, p. 81. *Anal.* E. G. Radley.
- VIII Dolomite, Machen Qy., Machen, Monmouthshire (Carboniferous). Average of 10 samples from different horizons. *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XVI, 1920, p. 86. *Anal.* E. G. Radley.

In the foregoing analyses, calculated carbonate compositions are as follows¹:

<i>Analysis</i>	<i>CaCO₃ (%)</i>	<i>MgCO₃ (%)</i>
I	94.80	0.67
II	95.30	0.67
III	93.99	1.25
IV	95.42	1.42
V	66.68	3.79
VI	74.96	16.52
VII	54.01	42.79
VIII	53.10	39.38

TABLE 14

ANALYSES OF CHALK (B1.5)

CONSTITUENT	I	II	III
SiO ₂	0.94	1.89	1.57
Al ₂ O ₃	0.24	0.35	0.27
Fe ₂ O ₃	0.15	0.15	0.13
FeO	—	—	—
MgO	0.48	0.36	0.53
CaO	54.79	54.39	54.48
Mn	0.04	0.033	0.03
Cu (p.p.m.)	5	4	6
Cl	0.008	0.005	0.003
P ₂ O ₅	0.04	0.043	0.058
SO ₃	0.066	0.028	0.033
Loss (1100°C.)	42.17	42.79	42.86
Totals (%)	100.09	100.04	—

¹ In these cases quoted, where the limestone sample contains significant amounts of minerals other than represented by calcium and magnesium carbonates, calculations must necessarily be regarded as approximate only.

TABLE 14—continued
ANALYSES OF CHALK (B1.5)

CONSTITUENT	I	II	III
Acid-insoluble	1.85	2.71	—
Acid-soluble Fe_2O_3	0.013	0.025	—
Acid-insoluble FeO	0.045	0.07	—
Water soluble	0.09	0.13	—

- I Chalk, S. England (Upper Cretaceous). R. C. Moakes, J. R. Pyne and D. C. Soul. *Whittings, Limestones and Precipitated Calcium Carbonate as Rubber Fillers*, (Research Assocs. Brit. Rubber Mnfrs. and Whiting Fed.), 1954, p. 5.
- II Chalk, N. England (Upper Cretaceous). R. C. Moakes, J. R. Pyne and D. C. Soul, *op. cit.*, p. 5.
- III Chalk, N. and S. England (Upper Cretaceous). R. C. Moakes, J. R. Pyne and D. C. Soul, *op. cit.*, p. 5. Mean of 9 analyses, 4 N. and 5 S. England.

Further analyses of chalk are given in Table 15 below:

TABLE 15

CONSTITUENT	IV	V	VI	VII	VIII
CaCO_3	98.40	94.09	97.25	85.91	98.52
MgCO_3	0.08	0.31	tr.	tr.	0.29
$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$	0.42	1.29	1.26	1.21	0.40
SiO_2 & insol.	1.10	3.61	0.65*	11.02†	0.65
Totals (%)	100.00	99.30	99.16	98.14	99.86‡

* This represents P_2O_5 , H_2Q at 100°C . and organic matter. SiO_2 and insoluble matter not determined.

† Insoluble residue (clay) made up of SiO_2 , 8.5%; $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, 1.51%; CaO , 0.28%; MgO , 0.29%; organic matter, 0.44%. The total also includes 0.66% moisture at 100°C .

‡ Actual total 100.04%, made up by CaSO_4 , 0.14%; MnO_2 , 0.04%, with traces of P_2O_5 and organic matter.

- IV Chalk with Flints, Shoreham, Sussex (Upper Cretaceous, Upper Chalk). J. Preswich, *Geology, Chemical, Physical and Stratigraphical*, (Oxford Clarendon Press, Oxford), 1886, p. 29. *Anal.* D. Forbes.
- V Chalk Rock, Newmarket, Suffolk (Upper Cretaceous, Upper Chalk). W. H. Penning and A. J. Jukes-Browne, *Mem. Geol. Surv.*, 51 S.W., 1881, p. 66. *Anal.* Dr. Frankland, F.R.S.
- VI Chalk, Francis Qy., Cliffe Creek, Cliffe-at-Hoo, Kent (Upper Cretaceous, Upper Chalk). W. Whitaker, *Mem. Geol. Surv.*, The Geology of London, I, 1889, p. 529. *Anal.* W. J. Ward.
- VII Grey Chalk, Folkestone, Kent (Upper Cretaceous, Middle Chalk). J. A. Howe, *The Geology of Building Stones*, (Edward Arnold, London), 1910, p. 183.
- VIII Chalk (Totternhoe Stone), Burwell, Cambridgeshire (Upper Cretaceous, Lower Chalk). W. H. Penning and A. J. Jukes-Browne, *op. cit.*, p. 43.

CHERT, FLINT (B2.1), AND SILICEOUS EARTH (DIATOMITE) (B2.3).—Both chert and flint are normally exceedingly pure siliceous rocks, the former usually composed of fibrous and/or radial chalcedony (frequently with silicified organic remains) and pre-Cretaceous in age, the latter made up of granular and/or opaline chalcedony, essentially belonging to chalk (Upper Cretaceous).

Chalcedony is a cryptocrystalline form of quartz (SiO_2); opaline chalcedony ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), *i.e.* the opal part, gives weak X-ray patterns of cristobalite ($4(\text{SiO}_2)$), low temperature, tetragonal phase; may be cristobalite in an amorphous, siliceous matrix¹. In pure SiO_2 , Si = 46.7%, O = 53.3%.

Analyses of British chert and flint are few and far between; in this respect these rocks differ from diatomite, which has at least received considerable international commercial attention, largely on account of its value in refractories manufacture (*e.g.* insulating bricks).

TABLE 16
ANALYSES OF CHERT (B2.1) AND
SILICEOUS EARTH (DIATOMITE) (B2.3)

CONSTITUENT	I	II	III	IV	V	VI	VII	VIII
SiO_2	95.84	95.50	69.64	73.06	83.77	73.01	78.92	62.19
Al_2O_3	1.97†	0.10	4.93	5.17	5.94	8.55	5.86	0.41
Fe_2O_3	} 0.70	1.95	3.98	4.18	5.12	2.09	2.14	1.90
FeO		0.15	—	—	—	—	—	—
MgO	0.12	tr.	1.89	1.98	2.28	0.83	0.41	0.56
CaO	0.37	—	1.53	1.60	1.84	1.14	0.84	1.05
Na_2O	0.14	tr.	0.35	0.37	0.43	} 0.28	0.59	} 0.14
K_2O	0.36	—	0.06	0.06	0.06		0.20	
$\text{H}_2\text{O} + 105^\circ\text{C}$.	—	—	11.77*	12.34*	—	7.71*	—	33.59*
$\text{H}_2\text{O} - 105^\circ\text{C}$.	—	—	4.69	—	—	6.39	4.98	—
TiO_2	0.13	—	0.50	0.56	0.61	—	0.32	—
CO_2	—	—	0.13	0.14	—	—	0.10	—
CaCO_3	—	0.87	—	—	—	—	—	—
SO_3	—	—	—	—	—	—	0.17	0.16
Cl	—	—	—	—	—	—	0.15	—
S	—	—	0.26	0.27	—	—	—	—
Loss on Ignition	—	1.43	—	—	—	—	5.75	—
Totals (%)	99.63	100.00	99.73	99.73	100.05	100.00	100.43	100.00

* Includes carbonaceous and/or organic matter.

† Includes ZrO_2 and P_2O_5 .

¹ M. H. Hey, *An Index of Mineral Species and Varieties*, (British Museum, London), 1950, p. 40.

- I Chert, Pilot Mountain, Mina, Nevada, U.S.A. (Trias). *U.S.G.S. Bull.* 878, 1937, p. 43. *Anal.* J. G. Fairchild.
- II Chert, Ireland (Upper Carboniferous). *Sci. Trans. Roy. Dublin Soc.*, 1, 1878, p. 85. *Anal.* E. T. Hardman.
- III Diatomite, Loch Cuithir, Skye, Scotland. Average 6 samples as received. *Anal. Geochemical Laboratories.*
- IV Diatomite, as III but average of same 6 samples moisture free. *Anal. Geochemical Laboratories.*
- V Diatomite, as III but average of same 6 samples calcined. *Anal. Geochemical Laboratories.*
- VI *Diatomite, N. Ireland. Raw Material Rep. Mineral Industry of Brit. Empire and Foreign Countries, (Imperial Institute), 1922.**
- VII Diatomite, Baker, Harney, Jefferson, Klamath and Malheur Counties, Oregon, U.S.A. *U.S.G.S. Bull.* 878, 1937, pp. 44-45. Average of 16 samples. *Anal.* E. T. Erickson.
- VIII Diatomite, Ordie Moss, Aberdeen, Scotland. (Moisture free). *Bull. Imp. Inst.*, 3, 1905, pp. 94-96. §
- ‡ Calcined material: SiO_2 , 85.00%; Al_2O_3 , 9.95%; Fe_2O_3 , 2.43%; CaO , 1.33%; MgO , 0.90%; alkalis, 0.33%.
- § Calcined material: SiO_2 , 93.36%; Al_2O_3 , 0.62%; Fe_2O_3 , 2.85%; CaO , 1.58%; MgO , 0.83%; alkalis, 0.21%; SO_3 , 0.24%.

In interpreting analyses of samples of diatomite, it is obviously important to know whether they represent raw material as dug, moisture-free material, or calcined earth. In Table 16 above, these differences are exemplified by figures given in columns III, IV and V. Impurities are invariably represented by hydrated aluminous silicates (Al_2O_3 and $\text{H}_2\text{O}+105^\circ\text{C}$. are pointers to these minerals), iron oxide (as Fe_2O_3) and usually to a lesser extent $\text{CaO}+\text{MgO}$. In calcining, such constituents as CO_2 , S, carbonaceous matter and $\text{H}_2\text{O}+$ are driven off. 'The composition of a pure diatom should be 94% silica, 6% water of hydration¹.'

CARBONACEOUS DEPOSITS (B4).—The three examples of these constitutionally variable and economically valuable deposits selected for chemical consideration here are Coal (B4.3), Oil-Shale (B4.5) and Asphalt (B4.6). Obviously from the individually distinctive nature of these materials both methods of analyses and results aimed at differ fundamentally from the sedimentary rocks previously discussed in this chapter.

With coal, apart from certain physical tests, technique is usually divided into (a) proximate and (b) ultimate analyses; (a) requires determination of moisture, volatile matter and ash; (b) requires determination of C, H, N, S, P, As and Cl. Analysis of coal ash is,

¹ H. Oliver, *The Development of Insulating Bricks for Furnace Construction. Ceramics*, (Brit. Ceramic Soc., Stoke-on-Trent), 1953, p. 597.

however, a silicate analysis is not sufficient for the analysis of that of siliceous sediments. Requirements for analysis of these current British Standards are SiO_2 , Al_2O_3 , Fe_2O_3 , Na_2O , K_2O , TiO_2 , MnO , SO_3 and P_2O_5 .¹

In the case of oil-shale, information sought can lead to even more comprehensive analysis than with coal. Everything depends on source, nature and economic circumstances of the shale under investigation. Fundamentally, we require to establish the fact that a sample of oil-shale is, indeed, oil-producing at commercial level; thus yield of crude oil in gallons/ton must first be established; characteristics of the crude product are determined, e.g. specific gravity and setting point; nature and characteristics of refined products from the oil; yield of ammonia. But these are essentially physical tests. Proximate analysis requires estimation of moisture, volatile matter, fixed carbon and ash; composition of ash is, like coal, a subject of direct silicate analysis. Add to all this, collateral determinations of S and N in the shale, sometimes C, H and C/H ratio, N equivalent to ammonia yield, and other commercially important properties, and it will soon be appreciated that oil-shale evaluation *de novo* or in the course of routine control of established raw material, crude oil and refined products, is a highly specialized technology wherever these deposits are economically worked; actual chemical analysis plays only a subsidiary role in the scheme as a whole.

With asphalts, we are only concerned here with native occurrences, e.g. Gilsonite or Trinidad Lake Asphalt, or naturally impregnated bituminous rocks, e.g. natural rock asphalts from France, Sicily or Switzerland. With these materials the approach is predominantly to establishing physical properties, characteristics of native bitumens, degree of impregnation (*i.e.* soluble bitumen) in rock asphalts. A purely chemical investigation of the hydrocarbons in these materials is of necessity decidedly academic and requires highly specialized knowledge of organic chemistry; it can never be reduced to the level of a routine operation.

The data given below on coal, oil-shale and asphaltic rocks, can only be regarded as a rough guide to information sought by chemical, petrographical and physical methods for their technical elucidation. In recent years great advances have been made in our knowledge of these hydrocarbons, by evolution of fundamentally correlated but highly integrated technologies appropriate to each of these materials; it is essential that the reader should consult the

¹ B.S.1016: 1042, Methods for the Analysis and Testing of Coal and Coke; also parts 1-5, 1957; part 6, 1958; parts 7-12, 1959.

extensive literature available; references quoted below are recommended as an introduction to the subject of carbonaceous deposits as a whole¹.

COAL (B4.3).—The example selected to illustrate the scheme of analysis involved with certain types of coal is quoted from the paper by F. V. Tideswell and R. V. Wheeler².

PROPERTIES OF COAL COMPONENTS FROM
HAMSTEAD SEAM

					<i>Vitrain</i>	<i>Clarain</i>	<i>Durain</i>	<i>Fusain</i>
Density	1.290	1.280	1.395	—
Ultimate analysis (% on ash-free dry coal)								
Carbon	78.5	79.1	80.8	84.7
Hydrogen	5.15	5.2	5.1	3.9
Oxygen	13.9	13.4	11.8	9.7
Nitrogen	1.33	1.28	1.3	1.05
Sulphur	1.12	1.02	1.0	0.65
Proximate analysis:								
Moisture (%)	12.6	10.2	6.5	3.9
Ash (%)	1.2	1.45	3.6	10.0
Volatile matter (% on ash-free dry coal)	38.6	40.8	39.4	22.6
Extractions (% on ash-free dry coal):								
By pyridine	34.4	27.2	21.6	10.1
By alcohol	6.6	5.7	3.1	—
By chloroform	2.85	—	2.4	—
Pyridine extract soluble in chloroform (%)	27.0	30.0	40.0	—
Percentages of α , β and γ compounds in the coal:								
α compounds	65.8	72.8	78.4	—
β compounds	25.0	19.0	13.0	—
γ compounds	9.2	8.2	8.6	—
Action of reagents (% on ash-free dry coal):								
Solubility in hot alcoholic potassium hydroxide	6.1	5.4	3.8	—
Iodine absorption (permanent):								
N/10 aqueous iodine in 24 hr.	22.8	23.6	17.8	4.3
Wijs's solution, in 6 hr.	67.9	63.2	51.3	4.3

¹ W. Francis, *Coal: Its Formation and Composition*, (Arnold, London), 1954.
D. J. W. Kreulen, *Elements of Coal Chemistry*, (Nijgh and Van Ditmar, N.V. Rotterdam), 1948.

H. H. Lowry and ors., *Chemistry of Coal Utilization*, 2 vols., National Research Council (Wiley, New York), 1945.

The Oil-Shales of the Lothians, 3rd ed., *Mem. Geol. Surv.*, Scotland, 1927. (See particularly Part III, Chemistry and Technology of the Oil-Shales.)

H. Abraham, *Asphalts and Allied Substances*, 5th ed., (Van Nostrand, New York), I and II, 1945.

D. C. Broome, *The Testing of Bituminous Mixtures*, (Arnold, London), 1934.

² *Journ. Chem. Soc.*, 115, 1919, p. 619.

OIL-SHALE (B4.5).—The chemical composition of Scottish oil-shale is conveniently summarized in the following table¹:

TABLE 17

SHALE	C %	H %	N %	S %	O By diff. %	Ash %	C/H ratio —
Good average*	25.27	3.67	1.14	0.49	5.65	63.74	6.89
Broxburn†	24.88	3.67	0.68	0.80	8.07	61.90	6.78
Dunnet‡	10.22	1.55	0.49	0.92	4.29	82.53	6.59
Camps§	13.11	2.10	0.53	0.24	—	71.25	6.24

* E. J. Mills, *Destructive Distillation*, 1892.

† J. B. Robertson, *Proc. Roy. Soc. Edin.*, 34, part ii, 1914, pp. 190–201.

‡ J. B. Robertson, *ibid.* Figures quoted refer to 'Top Foot'.

§ S. Allen, Scottish Shale Oil Scientific and Industrial Research Association, Glasgow, 1925. Figures quoted refer to 'Working Seam'.

In the above Table 17 'the carbon-hydrogen ratio C/H adopted by Strahan and Pollard (1908) as a basis for the classification of coals is applied by Robertson to oil shales. In all the shales examined, the ratio is lower than in ordinary bituminous coals, and the analyses show that the organic matter varies considerably in constitution'².

Some further data on yield of crude oil and percentage of volatile matter (which do not appear to be inter-related) are given in Table 18 below³.

TABLE 18

SAMPLE OF OIL-SHALE	YIELD OF CRUDE OIL		PERCENTAGE OF VOLATILE MATTER	PERCENTAGE OF CRUDE OIL IN THE VOLATILE MATTER
	GALLS. PER TON	PER CENT		
Greystone, above				
Lower Dunnet	50.46	19.60	34.90	56.16
Fells	48.79	19.06	35.71	53.37
Broxburn	29.61	11.57	36.23	31.93
Lower Dunnet	19.31	7.54	22.64	33.30
Upper Raeburn	15.01	5.86	22.81	25.69
Calmy Blaes, Upper Dunnet	4.65	1.81	15.76	11.48

¹ The Oil Shales of the Lothians, *Mem. Geol. Surv., Scotland*, 1927, p. 167.

² *Ibid.*, p. 167.

³ *Ibid.*, p. 168.

Finally, here are results of tests and analyses made on samples of 'No. 1 or Grey' Seam, Broxburn Shale, which illustrate the sort of comprehensive information sought on these rocks¹:

Crude Oil:	
Yield galls./ton	23·46
Sp. Gr.	0·876
Setting Pt.	87°F.
S/Ammonia (25%NH₃)	
Yield, lb./ton	61·59
Proximate Analysis:	
Moisture %	3·51
Volatile Matter %	22·79
Fixed Carbon %	1·76
Ash %	71·94
	<hr/> 100·00 <hr/>
Sulphur in Shale %	1·13
Nitrogen in Shale %	0·70
S/Ammonia (25%NH₃):	
Yield, lb./ton to which N is equiv.	76·18
Percentage recovered:	
As S/Ammonia	80·8
As N	80·8
Ash in Shale (as above)	
Composition: SiO ₂	47·87
Al ₂ O ₃	29·80
Fe ₂ O ₃	9·20
CaO	8·61
MgO	1·85
SO ₃	2·86
Cl	0·31
Na ₂ O	—
K ₂ O	—
Total %	<hr/> 100·50 <hr/>

ASPHALT (B4.6).—The examples chosen to illustrate materials in this category are the well-known Trinidad Lake Asphalt (native) and certain of the better known European natural rock asphalts.

¹ The Oil Shales of the Lothians, *Mem. Geol. Surv.*, Scotland, 1927, pp. 170, 171.

Raw asphalt as dug from the lake in Trinidad is an extremely uniform mixture of bitumen, mineral matter, water and other volatiles. Average analysis of the crude asphalt is as follows¹:

	<i>Per Cent.</i>
Water and gas volatilized at 100°C.	29.0
Asphalt soluble in CS ₂	39.0
Asphalt adsorbed by mineral matter	0.3
Mineral matter on ignition	27.2
Water of hydration in mineral matter	4.3
Total	<hr/> 99.8 <hr/>

The refined lake asphalt or 'Trinidad Epure' as exported from the island shows on analysis²:

	<i>Per Cent.</i>
Bitumen soluble in CS ₂	53.0-55.0
Free mineral matter	35.5-37.0
Water of hydration etc.	9.7

Chemical composition of mineral matter³:

SiO ₂	70.64
Al ₂ O ₃	17.04
Fe ₂ O ₃	7.62
CaO	0.70
MgO	0.90
Na ₂ O	1.56
K ₂ O	0.35
SO ₃	0.97
Cl	0.22
	<hr/> 100.00 ⁴ <hr/>

Natural rock asphalt is associated with such well-known localities as Val de Travers and Neuchatel, Switzerland; Seyssel and St. Jean, France; Limmer and Vorwohle, Germany; Ragusa, Sicily, names which have long been and still are by-words in the asphalt industry where building and road material specifications involving naturally impregnated rocks are mandatory. A few typical analyses are quoted here, but it should be noted that soluble

¹ H. Abraham, *Asphalts and Allied Substances*, 5th ed., (Van Nostrand, New York), 1, 1945, p. 199.

² H. Abraham, *op. cit.*

³ A. W. Attwooll and D. C. Broome, *Trinidad Lake Asphalt*, 2nd ed. (Baynard Press, London), 1954, p. 38.

⁴ *Anal.* C. Richardson (1908).

bitumen contents are today decidedly fluctuating and depend to a great extent on the horizon, precise locality from which supplies are drawn and, incidentally, the year when the analysis was made.

NEUCHÂTEL-VAL DE TRAVERS ¹	A %	B %	C %
Soluble in CS ₂	8.60	9.20	10.50
SiO ₂	0.09	0.14	0.32
Al ₂ O ₃ + Fe ₂ O ₃	0.38	0.30	0.23
CaO	54.95	55.00	54.98
MgO	0.06	0.07	0.15
CO ₂	43.71	43.31	42.85
Na ₂ O, K ₂ O SO ₃ + loss } Totals	0.81	1.11	1.47
	100.00	99.93	100.00

The name 'Seyssel' is traditionally associated with imports of natural rock asphalt to this country from Dept. of Ain (Pyrimont), France, as long ago as mid-nineteenth century (it had been exploited in France years before that). Average composition of *original* Seyssel material was as follows²:

SEYSSEL	PER CENT
Soluble in CS ₂	8.00-8.15
Insol. in acid	0.10-0.45
Al ₂ O ₃ + Fe ₂ O ₃	0.15
CaCO ₃	89.55-91.30
MgCO ₃	0.10
Water	1.9
Loss, etc.	0.10-0.20

Two other *original* analyses of well-known rock asphalts will serve to complete the picture³:

	VORWOHL %	RAGUSA %
Soluble in CS ₂	8.50	8.92
Insol. in acid	4.77	—
Al ₂ O ₃ + Fe ₂ O ₃	—	0.91
CaCO ₃	80.04	88.21
MgCO ₃	0.55	0.96
Undetermined	2.11	0.40
Sand	—	0.60

¹ H. Abrahams, *op. cit.*, p. 209.

² H. Abrahams, *op. cit.*, p. 207.

³ A. Danby, *Natural Rock Asphalts and Bitumens*, (Constable, London), 1913, p. 155.

PHOSPHATIC DEPOSITS (B5).—Under this heading is concerned phosphoric acid in various combinations, recognized petrographically in the form of phosphatic nodules, 'coprolites', phosphatic chalk and phosphorite (bedded massive apatite). The

TABLE 19
ANALYSES OF PHOSPHATIC DEPOSITS (B5)

CONSTITUENT	I	II	III	IV	V
SiO ₂	12.27	6.96	0.5	1.96	7.48
Al ₂ O ₃	3.72	1.78	0.8	} 1.01	{ 10.12
Fe ₂ O ₃	4.81	2.13	0.1		
MgO	1.34	0.88	—	0.12	0.28
CaO	38.20	45.06	53.7	53.24	36.45
Na ₂ O	1.18	0.71	0.2	} 0.19	0.43
K ₂ O	0.56	0.58	0.1		
H ₂ O + 105°C.	} 2.53	4.05	{ 0.7	—	—
H ₂ O — 105°C.				—	1.32
TiO ₂	—	—	—	—	0.45
P ₂ O ₅	24.24*	26.35†	11.6	11.66	31.00
CO ₂	5.37‡	5.76§	28.7	28.10	2.18
SO ₃	1.40	0.91	0.7	0.89	0.11
Cl	0.07	tr.	tr.	tr.	—
F	4.31	5.56	0.7	tr.	2.00
C	—	—	—	—	0.17
Org. Matter	—	—	2.3	2.83	—
Loss on Ignition	—	—	—	—	6.19
Totals (%)	100.00	100.71	100.1	100.00	100.75

* Equal to 52.52 % Ca₃(PO₄)₂. † Equal to 12.20 % CaCO₃.

‡ Equal to average 56.84 % Ca₃(PO₄)₂. § Equal to average 13.08 % CaCO₃.

|| Total, less Oxygen (0.83 %), 99.92 %.

- I 'Coprolites', Suffolk (Pliocene). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, V, 1916, p. 16 (average sample). *Anal. A. Voelcker.*
- II 'Coprolites', Cambridge (Cambridge Greensand). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, V, 1916, p. 18 (average 3 analyses). *Anal. A. Voelcker.*
- III Phosphatic Chalk, Taplow, Buckinghamshire (Upper Chalk). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, V, 1916, p. 17. *Anal. J. H. Player.*
- IV Phosphatic Chalk, Ciply, Belgium (Cretaceous). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, V, 1916, p. 17. *Anal. M. A. Petermann.*
- V Phosphorite, Florida, U.S.A. (Florida Phosphates). F. W. Clarke, *The Data of Geochemistry, U.S.G.S. Bull. 770*, 1924, p. 533. Average 4 analyses. *Anal. G. Steiger.*

criterion of economic value of naturally-occurring phosphates is the tricalcium phosphate (Ca₃(PO₄)₂) content (theoretical 45.8%)

P₂O₅) which in some Lower Greensand nodules reaches over 48%; Cambridge 'coprolites' (Cambridge Greensand), contain 55–60%; Suffolk 'coprolites' (Pliocene) range from 50 to 60%; phosphatic chalk (Upper Chalk) is restricted and uneconomic to work; the Taplow development yields about 11% P₂O₅. Phosphorite occurs in Ordovician rocks at Llanfyllin, Montgomeryshire, in a concretionary, graphitic bed which used to be worked; average Ca₃(PO₄)₂ content was about 46%, rising to 64% in the best concretions¹. The above chemical analyses (Table 19) are relevant.

CHEMICAL DEPOSITS (C).—Analyses in this group illustrate calcareous (C1), ferruginous (C2) and saline (C4) deposits. An example of (C1), is Dolomite (C1.2), whose composition when pure (previously noted p. 344) is, CaCO₃, 54.35%; MgCO₃, 45.65% of which in terms of CaO: MgO is 1:1.4. Pure dolomites are rare; usually CaO is in excess of theoretical CaO: MgO ratio; impurities are likely to be Al₂O₃, SiO₂, free or in combination as silicate, also Fe₂O₃. The theoretical composition of ideally pure dolomite, as would be shown by analysis, is CaO, 30.4%, MgO, 21.9% and CO₂, 47.7%. Judged by this yardstick, the following is a selection of dolomites used primarily in manufacture of basic refractory furnace linings:

TABLE 20

LOCALITY	CaO %	MgO %	CO ₂ %	ANALYST AND REFERENCES
Anston, Yorkshire	29.21	21.16	46.41	E. G. Radley‡
Harboro' Rocks, Brasington, Derbyshire*	30.65	21.33	42.17	H. Louis§
Duror, Argyllshire	30.72	19.97	45.28†	Stewarts and Lloyds
Durness, Sutherlandshire	29.65	21.53	46.62	W. Pollard¶
Skye, Inverness-shire	30.50	21.19	44.54	W. Pollardϕ
Binnenthal, Switzerland	29.90	22.21	47.77	—**
Sunk, Styria, Austria	30.19	21.07	42.52	—††
Wallowa Mts., Oregon, U.S.A.	32.84	20.52	46.60	J. G. Fairchild‡‡

* Average of 9 samples. † Loss on ignition: includes CO₂.

‡ *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, 16, 1920, p. 81.

§ *Op. cit.*, p. 90.

|| *Op. cit.*, p. 91.

¶ *Op. cit.*, p. 88.

ϕ *Op. cit.*, p. 88.

**†† Quoted in Dana's *System of Mineralogy*, 7th ed., (Wiley, New York), II, 1951, p. 212. See also full references to analyses, p. 217.

‡‡ R. C. Wells, *U.S.G.S. Bull.* 878, 1937, p. 59.

¹ *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, V, 1916, pp. 13–22.

BEDDED IRON ORES (C2.1).—The term ‘bedded’ as applied to iron ores means sedimentary rocks high in metallic iron content and forming part of an established stratigraphical sequence, thus differentiating them from ore-bodies (*e.g.* hematite) found in lodes, pipes, veins, etc., in varying types of country-rock, hence excluded from the scope of this chapter.

These mineralogically complex deposits, providing as they do today, the major proportion of indigenous iron ore in Britain, are born of both inorganic and organic parentage; genetically they do not fit comfortably into any systematic classification of sedimentary rocks¹. From a strictly chemical standpoint, however, mechanism of provenance matters little; it is composition in general (varying with stratigraphical horizon) and elemental iron-richness in particular, that accounts for the magnitude of published analyses extant of these rocks, both from official and commercial sources, from which, in the space available here, it is difficult to construct a truly representative cross-section of types. However, given a stratigraphical approach to the subject, there emerge some interesting comparative data which the accompanying sixteen chemical analyses serve to amplify (p. 360).

‘Ironstone analyses are commonly carried out either on the ore as submitted to the assayer or after it has been dried at 100°C. The procedure followed is indicated by the words “raw stone” or “ore as received” in the first case and by “dry” or “dried at 100°C.” in the second. Occasionally analyses are carried out on the ore after calcination². It is thus important to distinguish between analyses of raw stone, dried stone and calcined ore in the records. Throughout Table 21, p. 361, statements represent raw stone unless otherwise stated. Equivalent metallic iron contents to the sixteen analyses are tabulated separately (p. 363).

In interpreting chemical analyses of ironstones in terms of iron-bearing minerals, the following notes may prove helpful:—

Chamosite:	$2\text{SiO}_2 \cdot (\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3) \cdot 3(\text{FeO}, \text{MgO}) \cdot \text{Aq.}$ ³			
Mol. Ratios	200	102	200	292
	Equiv. Fe: 38%			
Goethite:	$4[\text{FeO} \cdot \text{OH}]$. Equiv. Fe: 62.9%.			
Hematite:	Fe_2O_3 . Equiv. Fe: 70%.			
Limonite:	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Goethite plus amorphous material.			
	Equiv. Fe: 60%.			
Magnetite:	Fe_3O_4 . Equiv. Fe: 72.4%.			
Pyrite:	FeS_2 . Equiv. Fe: 46.6%.			
Siderite:	FeCO_3 . Equiv. Fe: 48.2%.			

¹ See Vol. II, Ch. II.

² The Northampton Sand Ironstone, *Mem. Geol. Surv.*, 1951, p. 45.

³ The Liassic Ironstones, *Mem. Geol. Surv.*, 1952, pp. 18, 19.

**SUMMARY OF STRATIGRAPHICAL, PETROGRAPHICAL AND
CHEMICAL CHARACTERISTICS OF BRITISH BEDDED IRON ORES**

Geological Age	Formation	Type Locality	Petrography	Average Metallic Fe (%)	Average Essential Chemical Tendencies (%)
Lower Cretaceous	Lower Greensand	Seend, Wiltshire	Limonite oolite + siderite: 'iron-pan'	40	FeCO ₃ 37 Fe ₂ O ₃ 17 FeO 2 SiO ₂ 22
Lower Cretaceous	Wealden	Wadhurst and Ashburnham, Sussex	Siderite mudstone ('clay ironstone')	30	FeCO ₃ 60 SiO ₂ 16
Lower Cretaceous	Claxby Ironstone (Wealden)	Claxby, Lincolnshire	Limonite oolite	38	Fe ₂ O ₃ 56 H ₂ O + 11 SiO ₂ 11
Upper Jurassic	Kimmeridgian	Abbotsbury, Dorset	Limonite oolite	35	Fe ₂ O ₃ 60 H ₂ O + 11
Upper Jurassic	Upper Corallian	Westbury, Wiltshire	Limonite oolite with chamosite, siderite	33	Fe ₂ O ₃ 42 FeCO ₃ 24 SiO ₂ 13 Al ₂ O ₃ 6
Upper Jurassic	Kellaways Beds (Callovian)	Fredville Boring, nr. Dover, Kent	Limonite oolite + sand	36	Fe ₂ O ₃ 32 FeO 17 H ₂ O + 12 SiO ₂ 17
Middle Jurassic	Northampton Sand Ironstone	Stanton, Irchester, Irthlingborough, etc. Northamptonshire	Chamosite oolite and siderite mudstone	33	Fe ₂ O ₃ 11 FeO 33 SiO ₂ 8 Al ₂ O ₃ 6 CaO 7 CO ₂ 21
Lower Jurassic	Upper Lias	Raasay, Invernesshire	Chamosite oolite	25	Fe ₂ O ₃ 2 FeO 30 SiO ₂ 6 Al ₂ O ₃ 6 CaO 17 CO ₂ 28
Lower Jurassic	Middle Lias	Banbury, Oxfordshire	Sideritic chamositic chamosite limestone	24	Fe ₂ O ₃ 35 CaO 20 SiO ₂ } 13 Al ₂ O ₃ }
Lower Jurassic	Lower Lias	Scunthorpe, Lincolnshire	Limonite oolite	22	Fe ₂ O ₃ 70 CaO 16 Insol. 13
Upper Carboniferous	Middle Coal Measures	Bassey Mine, N. Staffordshire	'Blackband' (argillaceous carbonates)	37	FeO 45 CO ₂ 33 SiO ₂ 2
Ordovician	Glenkiln Series	Dolgelley, Merionethshire	Pisolithic iron ore	35	FeO 28 Fe ₂ O ₃ 20 SiO ₂ 23 CaO 7

TABLE 21

ANALYSES OF BEDDED IRON ORES (B3 and C2)

CONSTITUENT	I	II	III	IV	V	VI	VII	VIII
SiO ₂	21.61	6.46	17.26	42.60	16.00	17.42	4.42	13.4
Al ₂ O ₃	5.82	2.64	6.45*	—	4.70	8.20	5.40	7.4
Fe ₂ O ₃	17.48	6.85	52.86	43.97	7.86	31.86	1.20	8.5
FeO	25.69	42.08	—	—	42.41	17.10	45.14	31.9
MgO	0.59	1.76	1.57	1.40	2.13	2.13	3.69	2.5
CaO	2.88	3.87	2.00	tr.	5.90	4.58	6.03	6.1
Na ₂ O	0.14	—	—	—	—	—	—	—
K ₂ O	0.83	—	—	—	—	—	—	—
H ₂ O+105°C.	3.05	tr.	10.48	} 11.88	—	—	—	3.6
H ₂ O-105°C.	2.59	0.15	5.68		—	—	0.14	4.9
TiO ₂	0.25	0.21	—	—	—	—	—	—
P ₂ O ₅	0.96	0.65	0.24	—	1.103	1.12	0.11	2.8
MnO	0.52	2.32	*	—	0.22	0.27	0.18	—
CO ₂	16.68	32.70	2.94	—	—	—	33.06	17.4
SO ₃	—	0.20	tr.	—	0.666	—	0.09	—
Cl	—	—	—	tr.	—	—	—	—
S	—	—	—	—	—	—	0.11	0.5
FeS ₂	0.50	0.11	—	—	—	—	0.03	—
Org. Matter	0.79	—	—	—	—	—	—	—
Loss on Ignition	—	—	—	—	19.20	17.50	—	—
Totals (%)	100.38	100.00	99.48	99.85	100.189	100.18	99.60	99.0

* This figure (Al₂O₃) includes MnO.

- I Ironstone, Seend, Wiltshire (Lower Greensand). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XXIX, 1925, p. 89.
- II Clay Ironstone, Ashburnham, Sussex (Wealden). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XII, 1920, p. 227. *Anal. R. R. Tatlock and —. Thompson.*
- III Claxby Ironstone, Acre House Mine, Claxby, Lincolnshire (Lower Cretaceous). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XII, 1920, p. 214. *Anal. J. D. Kendall.*†
- IV Abbotsbury Ironstone, Abbotsbury, Dorset (Kimmeridgian, Upper Jurassic). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XII, 1920, p. 223. *Anal. E. Riley.*
- V Westbury Ironstone, Westbury, Wiltshire (Upper Corallian, Upper Jurassic). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XII, 1920, p. 219.
- VI Fredville Ironstone (Limonite Oolite), Fredville Boring, Dover, Kent (Kellaways Beds, Callovian, Upper Jurassic). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XII, 1920, p. 226. *Anal. E. O. F. Brown.*

† Air-dried sample.

M*

- VII Northampton Sand Ironstone (Siderite Mudstone), Stanton, Corby, Northamptonshire (Inferior Oolite, Middle Jurassic). J. H. Taylor, *Petrology of the Northampton Sand Ironstone Formation*, *Mem. Geol. Surv.*, 1949, p. 61. *Anal.* Stewarts and Lloyds Ltd.
- VIII Northampton Sand Ironstone (Oolites with Siderite, Chamosite Matrix), Irchester, Northamptonshire (Inferior Oolite, Middle Jurassic). J. H. Taylor, *Petrology of the Northampton Sand Ironstone Formation*, *Mem. Geol. Surv.*, 1949, p. 60. *Anal.* G. A. Sergeant.

TABLE 22

ANALYSES OF BEDDED IRON ORES (B3 and C2), CONTD.

CONSTITUENT	IX	X	XI	XII	XIII	XIV	XV	XVI
SiO ₂	8.58	8.9	13.5	5.15	8.23	3.30	22.80	26.20
Al ₂ O ₃	4.24	7.9	10.2	4.49	4.26	1.42	8.64	15.71
Fe ₂ O ₃	1.24	39.1	3.0	69.93	0.69	1.14	20.00	3.70
FeO	11.79	—	32.5	0.95	46.30	41.65	27.64	28.45
MgO	1.71	0.8	3.5	1.05	2.08	2.16	2.10	1.36
CaO	35.43	16.6	5.0	0.57	2.30	4.20	6.50	6.50
Na ₂ O	0.08	—	—	0.01	—	—	—	—
K ₂ O	0.02	—	—	0.32	0.33	—	—	—
H ₂ O+105°C.	4.44	—	2.9	11.89	0.81	—	—	} 7.90
H ₂ O-105°C.	1.37	3.1	8.0	2.07	0.28	—	—	
TiO ₂	0.28	0.3	0.3	1.05	—	—	—	0.10
P ₂ O ₅	1.68	0.5	1.0	1.23	0.50	0.65	3.69	3.93
MnO	0.65	0.2	0.7	0.48	0.82	1.58	0.465	1.67
CO ₂	27.54	—	19.0	0.48	31.68	30.55	—	3.00
SO ₃	0.15	—	—	—	0.11	0.89	—	—
S	—	0.1	0.2	—	—	—	1.045	—
FeS ₂	0.72	—	—	—	0.08	—	—	1.39
Fe ₇ S ₈	0.15	—	—	—	—	—	—	—
Cr ₂ O ₃	nt. fd.	0.1	—	—	—	—	—	—
V ₂ O ₅	—	tr.	—	—	—	—	—	—
NiO	} 0.04	—	—	0.03	—	—	—	—
CoO		—	—	—	—	—	—	—
BaO		nt. fd.	—	—	—	—	—	—
Li ₂ O		nt. fd.	—	—	—	—	—	—
C	0.26	—	—	0.41	—	—	—	—
Org. Matter	—	—	0.2	—	0.62	12.70	—	—
Loss on Ignition	—	22.1	—	—	—	—	6.70	—
Totals (%)	100.37	99.7	100.00	100.11	99.19	100.24	99.58	99.91

- IX Raasay Ironstone, Main Mine, Raasay, Inverness-shire, Scotland (Upper Lias). *Mem. Geol. Surv., Summary of Prog.*, 1915 (1916), p. 28. *Anal.* E. G. Radley.
- X Marlstone Rock-Bed, Banbury Ironstone Field, Oxfordshire (Middle Lias). The Liassic Ironstones, *Mem. Geol. Surv.*, 1952, p. 201. *Anal.* G. A. Sergeant.
- XI Iron Ore (Chamositic Sideritic Chamosite Oolite), Main Seam, Cleveland, Yorkshire (Middle Lias). The Liassic Ironstones, *Mem. Geol. Surv.*, 1952, p. 61. *Anal.* J. E. Stead. (Average analysis.)
- XII Limonite Oolite (Frodingham Ironstone). Scunthorpe, Lincolnshire (Lower Lias). The Liassic Ironstones. *Mem. Geol. Surv.*, 1952, p. 76. *Anal.* F. R. Ennos, R. Sutcliff.
- XIII Iron Ore, Blue Flats, Donnington Wood, Coalbrookdale, Shropshire (Coal Measures). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XIII, 1920, p. 93.
- XIV Blackband Ironstone, Bassey Mine, N. Staffordshire (Middle Coal Measures). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XIII, 1920, p. 84.
- XV Bedded Pisolitic Iron Ore, Cross Foxes Mine, Dolgelley, Merionethshire (Ordovician). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XIII, 1920, p. 28. Average of large number of analyses by *Brymbo Steel Co.*
- XVI Oolitic Iron Ore, Llangoed, Anglesey, Wales (Ordovician). *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, XIII, 1920, p. 14. *Anal.* H. Greenwood.

TABLE 23

EQUIVALENT METALLIC IRON CONTENTS*

ANALYSIS NO.	Fe (PER CENT.)
I	32.42
II	37.55
III	36.97
IV	30.75
V	38.47
VI	35.57
VII	35.95
VIII	30.70
IX	10.48
X	27.40
XI	27.36
XII	49.65
XIII	36.51
XIV	33.09
XV	35.46
XVI	25.35

*Recalculated by A. H. Clarke.

CHLORIDES (C4.1).—Halite (rock-salt) as pure mineral NaCl contains 39.4% Na and 60.6% Cl. A saturated solution of salt in distilled water contains 26.42% NaCl at 15.5°C. '... ordinary water acting upon rock-salt dissolves from 23–25% of sodium chloride, that is, 1,000 gallons of water takes up 27 to 29 cwts., and 1,000 gallons of brine yields from 20 to 22 cwts. of salt'¹. Here are some typical analyses of British halites²:

TABLE 24

	A %	B %	C %	D %	E %
NaCl	99.00	94.36	89.14	99.09	98.42
MgCl ₂	0.13	0.09	0.62	0.10	0.12
CaCl ₂	—	—	—	0.03	—
CaSO ₄	0.28	1.23	1.69	0.30	0.21
Na ₂ SO ₄	—	—	—	—	—
NaHCO ₃	0.01	tr.	—	—	—
Insol.	0.65	4.49	0.11	0.27	1.15
Total (%)	100.07	100.17	100.00*	100.00†	100.00†

* Includes 8.44% moisture and 'undetermined'.

† Includes 0.10% moisture; insoluble is red clay.

‡ Includes 0.06% Al₂O₃ + Fe₂O₃ and 0.15% moisture.

A Adelaide Mine, Marston, Northwich.

B Same locality as A, average 6 analyses.

C Puriton, Somerset (borehole).

D Point of Ayre. Isle of Man (borehole).

E Salt Holme Farm, Port Clarence, Middlesbrough (borehole).

SULPHATES (C4.2) are always interesting deposits chemically and economically; commonly occurring members in sedimentary environments are gypsum CaSO₄ · 2H₂O, anhydrite CaSO₄, barite BaSO₄ and celestite SrSO₄.

In gypsum CaO, 32.57%, SO₃, 46.5%, H₂O, 20.93% represent pure mineral. In anhydrite CaO is 41.19%, SO₃, 58.81%. Barite comprises BaO, 65.70% and SO₃, 34.30%. Celestite is SrO, 56.42% and SO₃, 43.58% pure mineral. Following analyses are typical:—

¹ R. L. Sherlock, *Mem. Geol. Surv., Spec. Rep. Min. Res. Gt. Brit.*, **18**, 1921, p. 7.

² All analyses quoted are by R. L. Sherlock, *ibid.*, p. 8.

(I) Gypsum, Keuper Marl, Balderton, Nottinghamshire¹.

	%
CaSO ₄ .2H ₂ O	98.25
SiO ₂	0.42
Al ₂ O ₃ + Fe ₂ O ₃	0.33
MgO	0.30
Na ₂ O + K ₂ O	0.16
H ₂ O - 105°C. and organic matter	0.54
Total	100.00

(II) Gypsum, Keuper Marl, Yate, Gloucestershire².

	%
CaSO ₄	72.24
SiO ₂	0.98
Al ₂ O ₃ + Fe ₂ O ₃	0.41
CaCO ₃	2.76
H ₂ O +	19.80
Unestimated	3.81
Total	100.00

Anal. C. J. Waterfall.

(III) Anhydrite, Billingham Mine, Co. Durham³.

	%
CaSO ₄	89.9
SiO ₂	3.9
Al ₂ O ₃ + Fe ₂ O ₃	0.5
NaCl	0.085
H ₂ O	3.5

(IV) Barite, Racalmuto, Sicily⁴.

	%
BaO	65.06
SrO	0.17
CaO	0.25
SO ₃	34.51
Rem.	0.11
Total	100.10

This is equivalent to 99.02% BaSO₄.

¹ R. L. Sherlock and S. E. Hollingworth, *Mem. Geol. Sury., Spec. Rep. Min. Res. Gt. Brit.*, 3rd ed., 3, 1938, p. 41.

² *Ibid.*, p. 37.

³ *Ibid.*, p. 36.

⁴ Dana's *System of Mineralogy*, 7th ed., (Wiley, New York), II, 1951, .411, and other analyses there cited.

(V) Celestite, Djebel Kebbouch, Tunis¹.

	%
SrO	56.20
CaO	0.40
SO ₃	43.40
<hr/>	
Total	100.00
<hr/>	

(VI) Baryto-celestine, Chipping Sodbury, Gloucestershire².

	%
BaO	24.48
SrO	31.89
CaO	1.22
SO ₃	39.03
Fe ₂ O ₃ *	1.26
Loss on ignition	1.81
<hr/>	
Total	99.69 <i>Anal.</i> W. Pollard.
<hr/>	

* State of oxidation not determined.

¹ *Ibid.*, p. 417.

² R. L. Sherlock and S. E. Hollingworth, *op. cit.*, p. 77.

CHAPTER IX

MICROCHEMICAL METHODS OF MINERAL ANALYSIS

Christina C. Miller, PH.D., D.SC., F.H.-W.C., F.R.S.E.

Introduction—Qualitative Methods—Organic Reagents and Metal Ions—Selective Reactions—Analysis of Small Samples by Drop Reactions and Spot Tests—Systematic Analysis—Apparatus—Use of Centrifuge Cones—Miscellaneous Accessories—Confirmatory Tests and Estimations of Quantity—Mineralogical Applications—Semiquantitative Tests—Paper Chromatography—Ion Exchange—Quantitative Methods—The Microchemical Laboratory—Weighing—Disintegration of Minerals—Gravimetric Processes—Filtration—Drying and Ignition of Precipitates—Titrimetric Processes—Applications of Gravimetric and Titrimetric Methods in Mineral Analysis—Photometric Methods—Some Applications of Photometric Methods—Electrochemical Methods—Potentiometry—Polarography—Amperometric Titrations—Microchemical Combustion Methods.

INTRODUCTION

MICROCHEMICAL analysis relates essentially to examination of small samples of material of the order of 1 mg. to 10 mg. in weight. Sometimes, however, as in trace determination, an analysis may be started with a comparatively large sample and, by appropriate means, the minor constituent concentrated or isolated, so that the final part of the analysis is microchemical. Except when detection of traces is in question, and provided that sampling is adequate, systematic qualitative analyses are now usually made on small samples of material, whether or not ample is available, whereas a quantitative micro-analysis is done more likely because of paucity of material. For example, in sediments where the bulk material is commonplace but small amounts of heavy minerals may be of unusual interest, the latter may not always be readily identified microscopically and thus require quantitative chemical examination. Similarly, small amounts of hard minerals present as discrete particles within clays may have to be picked out for detailed investigation. Again, where inclusions in a material are a potential source of error, the error is likely to be a minimum when analyses are

performed on small fragments or grains seen microscopically to be uncontaminated.

When part only of a specimen is taken for micro-analysis, it is extremely important, in quantitative work especially, to ensure uniformity of the material by thorough mixing and arranging that the diameter of all particles is below a certain limiting size¹.

QUALITATIVE METHODS

The rapid detection of the constituent elements of materials has ever been a desideratum. As new elements were discovered and the well-known method of systematic chemical analysis for the common metals proved to be inadequate, A. A. Noyes and W. C. Bray and their associates began researches which enabled them to present a new scheme for practically all the metallic elements in very varied proportions². Detailed instructions are given for the treatment of all kinds of inorganic materials. While these researches were in progress, F. Emich³, in pioneering work, demonstrated that classical chemical operations could be scaled down and related to milligram (mg.) and microgram (μ g.) quantities. F. Emich's technique was employed by N. Schoorl⁴ for systematically detecting the common metals, also by A. Benedetti-Pichler and his co-workers⁵ for reducing A. A. Noyes and W. C. Bray's system to the micro-scale. For confirmation of the metals in the tiny precipitates, both freely employed the microscopic crystal tests evolved earlier by H. Behrens⁶ and his predecessors. These methods are not rapid and considerable skill is required in effecting the many separations. Of great interest, therefore, are the radical changes that have taken place in inorganic micro-analysis as a result of the widespread introduction of sensitive, selective organic reagents, and new methods of separation, such as solvent extraction and partition chromatography.

ORGANIC REAGENTS AND METAL IONS

The electron-donating property of nitrogen, oxygen and sulphur atoms is retained in organic substances, which may co-ordinate

¹ B. Baule and A. Benedetti-Pichler, *Zur Probenahme aus kornigen Materialien*, *Zeit. anal. Chem.*, **74**, 1928, p. 442.

² *A System of Qualitative Analysis for the Rare Elements*, (Macmillan, London), 1927.

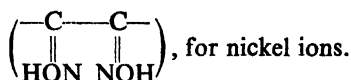
³ *Lehrbuch der Mikrochemie*, (Bergman, Wiesbaden), 1911.

⁴ *Zeit. anal. Chem.*, **46**, 1907, p. 658; **47**, 1908, pp. 209, 367 and 729; **48**, 1909, pp. 209, 401, 593 and 665.

⁵ *Mikrochem.*, **19**, 1935-36, pp. 1 and 239; **24**, 1938, p. 16; *Molisch-Festschrift*, 1936, pp. 3 and 36; *verein. mit Mikrochim. Acta*, **33**, 1948, p. 281; *Ind. Eng. Chem. (Anal.)*, **9**, 1937, p. 589; **10**, 1938, p. 107; **11**, 1939, pp. 117 and 294.

⁶ *A Manual of Microchemical Analysis*, (Macmillan, London), 1894.

with metal ions and form co-ordination compounds. If two or more donor groups in one molecule are available for co-ordination, then one or more rings may be formed, whereby a chelate compound results. Those metal chelates in which the co-ordination number of the metal is satisfied and the positive charge on the metal ion is neutralized by negative charges on some of the donor groups, are known as inner complex salts. They have important properties. Many are of striking and intense colour, great stability, definite constitution and low metal content; often they are sparingly soluble in water and readily soluble in organic solvents. Most important of all, certain atomic groupings in the molecules, irrespective of the groups, aliphatic, aromatic, or heterocyclic, attached to them, show a remarkable affinity for combination with particular metal ions. The classical example is the affinity of the α -dioxime grouping,



Other groups or atoms contained in organic reagent molecules affect the colour and the solubility of their complexes with metals, and the sensitivity and selectiveness of the salt formation. To some extent a molecule containing a selective grouping may be tailored to produce a desired effect. Thus larger substituents may be introduced in order to get bulkier precipitates, chromophoric groups to provide colour not already there, or solubilizing groups to render water-insoluble reagents or reaction products soluble. The name of F. Feigl¹ is pre-eminently linked with the search for the selective groupings and attachments most effective for particular metal ions.

SELECTIVE REACTIONS

Maximum selectivity in a reagent results when conditions of its reactions are suitably controlled with respect to pH value, temperature, valency state of the elements and suppression of unwanted reactions involving other ions. Mere oxidation or reduction of an ion may sometimes facilitate a desired reaction or suppress a potentially interfering one. The masking or the prevention of interference without physical separation, by means of fluoride, phosphate, cyanide, thiocyanate and various organic acids, is well-known; these combine with the ions they hold back, forming soluble complexes of greater stability than those formed between the interfering elements and the reagent under consideration.

Now metal chelates, especially inner complexes, are very stable,

¹ *Chemistry of Specific, Selective and Sensitive Reactions*, translated by R. E. esper, (Academic Press, New York), 1949.

and if they are water-soluble, then the reagents responsible for their formation may also be used as masking agents, sometimes in a highly selective manner. Prominent among new complexing agents are the aminopolycarboxylic acids, the 'complexones', the best-known of which, ethylenediaminetetra-acetic acid¹, forms very stable complexes with almost all metal ions that have a charge more than one.

Another important means of improving selectivity and sensitivity in reactions is to extract coloured metal chelates from aqueous solutions with organic solvents. In this way, trace metals invisible in otherwise coloured solutions may, under favourable conditions, be isolated and concentrated and thus made visible. Solvent extraction² is also being increasingly used as a substitute for troublesome separations of inorganic species by precipitation.

In spite of all that has been accomplished, there are still many metals for which suitable reactions of the nature described have not yet materialized and there are no comparable reactions for non-metallic elements. Sensitive tests, organic or inorganic in nature, particularly those based on colour production, have therefore been sought in other directions. Such effects as oxidation-reduction, adsorption, especially lake-formation, catalysis and fluorescence, have all been utilized and today there is probably no element for which a sensitive, if not a selective test, has not been found. A wide range of these is given by F. Feigl³.

ANALYSIS OF SMALL SAMPLES BY DROP REACTIONS AND SPOT TESTS

A sensitive test may provide sufficient material in a drop of solution to give an adequate reaction on a spotting tile or a filter paper and a selective reaction may permit direct detection of a particular element in the presence of many others. If sensitive specific reactions, permitting detection of individual elements in the presence of large excesses of any others, were eventually found for all the elements, analysis of a mixture would involve merely the application of a series of direct tests to successive small portions of the

¹ G. Schwarzenbach, *Complexometric Titrations*, translated by H. Irving, (Methuen, London), 1957; F. J. Welcher, *The Analytical Uses of Ethylenediaminetetraacetic Acid*, (Van Nostrand, New York), 1957; T. S. West and A. S. Sykes, *Analytical Applications of Diamino-ethane-tetra-acetic Acid*, (British Drug Houses Ltd, Poole, Dorset, England), 1959.

² G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*, (Wiley, New York), 1957.

³ *Spot Tests in Inorganic Analysis*, F. Feigl, translated by R. E. Oesper, (Elsevier, Amsterdam), 1958.

solution. Since this goal is not yet in sight, separations must still be an important factor in the examination of complex materials. When, however, one is thoroughly conversant with the scope and limitations of reactions, direct tests may be justifiably applied to materials whose origin and composition are not entirely unknown.

SYSTEMATIC ANALYSIS

In systematic testing for metals, a suitable choice of sensitive selective reactions enables one to reduce the amount of substance taken for examination, the number of groups into which the metals are separated, and the number of separations within the groups. Weaknesses of most schemes of micro- and semimicro-analysis are the exclusion of some or all rarer metals and failure to allow for very variable proportions of the metals. When complex minerals or their mixtures are in question, A. A. Noyes and W. C. Bray's¹ method of attack would still seem to be the best. A. Benedetti-Pichler and his co-workers², while retaining the essential features of this method in the analysis of 1 mg. of material, failed to simplify the course of separations. C. C. Miller³, with A. J. Lowe and R. J. Magee, succeeded in simplifying much of A. A. Noyes and W. C. Bray's scheme, in accordance with the concepts described above, giving much information about the range of application of the various tests. The maximum weight of sample usually represented 50 mg. of cations, but many tests were truly in the microchemical range. There is little doubt that the substitution of some more recent reactions for certain elements that at the time presented difficulties, will permit full analyses to be done on much smaller samples.

A good deal of information about microchemical tests suitable for a majority of the elements, including the non-metallic elements in various anionic states, is given by G. Charlot⁴ and by P. E. Wenger, R. Duckert and Y. Rusconi⁵. A. I. Vogel⁶ covers a limited number of elements. Other important sources of information are 'Tables of Reagents for Inorganic Analysis'⁷ and F. J. Welcher's

¹ *Op. cit.*

² *Loc. cit.*

³ *Journ. Chem. Soc.*, 1940, pp. 1258 and 1263; 1941, pp. 72 and 786; 1943, p. 72; 1947, p. 1347; 1951, pp. 3183 and 3188.

⁴ *Qualitative Inorganic Analysis*, translated by R. C. Murray, (Methuen, London), 1954.

⁵ *Traité de Chimie Analytique Qualitative Minérale*, (Georg, Genève), 1946.

⁶ *A Text-book of Macro and Semimicro Qualitative Inorganic Analysis*, 4th ed., (Longmans, Green, London), 1954.

⁷ First Report of the International Committee on New Analytical Reactions and Reagents of the Union Internationale de Chimie, (Akademische Verlagsgesellschaft, Leipzig), 1938; Third Report, (Librairie Istra, Paris), 1948.

four volumes on *Organic Analytical Reagents*¹. The examination of mg. amounts of insoluble matter has been given detailed consideration by F. Feigl². For those whose interests lie in the direction of crystal tests, É. M. Chamot and C. W. Mason's³ books should be consulted.

APPARATUS

The apparatus to be described is intended to cover requirements in systematic analysis as well as in direct testing procedures. Apart from an electrically-driven centrifuge, capable of taking centrifuge cones ranging in capacity from 0.5 to 15 ml., only small test-tubes and simple equipment are needed. Liquid reagents are stored in 1 or 2 oz. glass bottles, fitted, where practicable, with dropper pipettes. For certain reagents, polythene bottles and droppers are excellent. Solids are kept in little vials and portions removed by means of a spatula, made by beating out one end of a piece of 1 to 2 mm. diameter nickel-silver or platinum wire.

Small porcelain crucibles (1 to 4 ml.) and basins (10 ml.), glass beakers (6 ml.) and cover glasses, spotting tiles, graduated pipettes (0.1, 0.2, 0.5 and 1 ml.), a micro-Bunsen burner, also stainless steel forceps, are all easily obtained. For mineral analysis, a small platinum crucible and lid and a platinum spoon are desirable, the latter for fusions involving more material than would normally be dealt with in a platinum wire loop. A few tests may require the use of a microscope and a quartz lamp. Numerous other items can be bought but are easily made to suit individual requirements. They are referred to below,

USE OF CENTRIFUGE CONES

Small cones are seldom heated in flames because they are apt to crack and their contents are liable to bump, but are instead inserted in a beaker of boiling water, provided with a cover in which are holes of appropriate size. If higher temperatures are required, an aluminium heating block, in which holes have been drilled to accommodate the tubes, is suitable (Fig. 40). Gas or electrical heating is used.

Evaporations are expedited by allowing a current of purified air, supplied through a capillary tube, to play upon the surface of the solution. Group precipitates are usually formed in centrifuge cones. Liquid reagents are added from capillary dropper pipettes,

¹ Van Nostrand, New York, 1947.

² *Op. cit.*

³ *Handbook of Chemical Microscopy*, vol. I, 3rd. ed., (Chapman and Hall, London), 1958.

gases delivered through fine capillaries and the contents of tubes stirred with thin glass rods. After a precipitate has been centrifuged down, the solution is conveniently removed by means of either a bent pipette (Fig. 41B) or a capillary pipette with a teat. The capillary

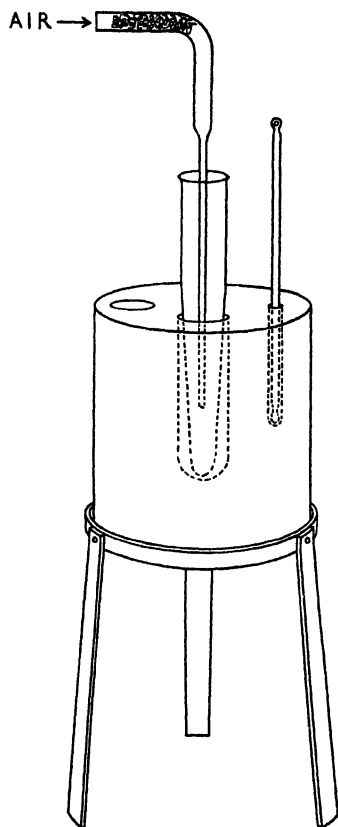


FIG. 40. Heating Block.

stem of the former is carefully lowered into the liquid until the tip is within 2 mm. of the precipitate. The solution is slowly withdrawn by mouth suction and the pipette, prior to its removal, sealed with the tip of the tongue. The bent pipette is also excellent for separating two liquid layers from each other in solvent extraction procedures.

MISCELLANEOUS ACCESSORIES

When liberation of a gas prevents settling of a precipitate, or a suspension in a crucible or on a spotting tile has to be filtered, a microfilter (Fig. 41A) is of value for collecting the liquid phase. A short 1 to 2 mm. capillary is drawn from 6 mm. diameter glass tubing and cut so as to leave a slightly fluted end into which a $\frac{1}{8}$ in. roll of filter paper is fitted and the excess cut off. The capillary is held vertically in the suspension and the liquid collected above

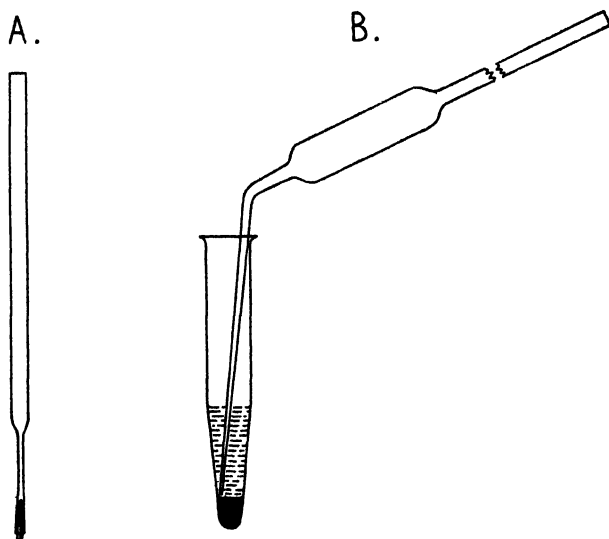


FIG. 41. Separation of Supernatant Solution.

A Micro filter.

B Withdrawal of centrifugate by bent pipette.

the paper by mouth suction. The apparatus shown in Fig. 42 are useful, particularly in testing for acid radicals, where collection and examination of volatile products are frequently required. In A, a small roll of filter paper in the inner tube, treated with lead acetate solution, will show the presence of sulphuretted hydrogen, liberated by acid treatment of a sulphide in the wider tube. In B, a fine glass hook will hold a fragment of litmus for detection of an acid or an alkaline vapour. In C, a ring of nickel wire will hold a film of lime water or phenolphthalein-sodium carbonate reagent for detection of carbon dioxide, or of water for hydrolysis of

silicon tetrafluoride, liberated by interaction of a fluoride with silica and sulphuric acid. A useful distilling flask, which prevents carry-over of material from the flask and permits collection and testing of the distillate in the side-tube, is shown in D.

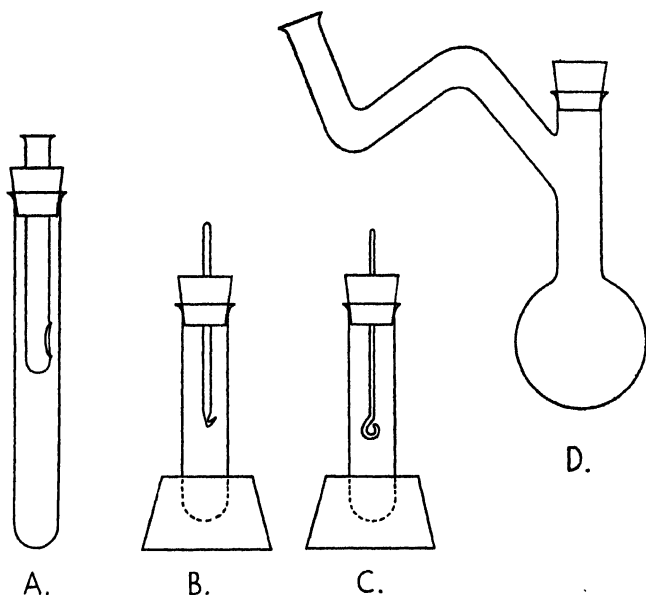


FIG. 42. A, B and C—Gas or Vapour Detection Outfits.
D.—Distillation Outfit.

CONFIRMATORY TESTS AND ESTIMATIONS OF QUANTITY

Graduated capillary pipettes may be used for measuring the small volumes to be tested. Sample and standard solution for comparison must be prepared in the same way. Sometimes a precipitate from a test solution may have to be dissolved and re-formed because other substances in the solution interfere with the bulk. In comparing coloured solutions, concentrations should be within the range of reasonable conformity to Beer's law. The concentrations of fluorescing substances must be below those at which self-quenching begins.

Reactions involving comparison of coloured solutions may be carried out on spotting tiles, in porcelain crucibles or basins, in centrifuge cones or test tubes, depending on their nature. Precipitates to be compared for bulk are formed in narrow centrifuge cones. In colorimetric precipitation tests made on absorbent paper,

test solution and reagent solution may be brought together, or the former applied to reagent-impregnated paper (Whatman drop reaction paper No. 120, 3MM and Nos. 42 and 542, or their equivalents). As irregular spreading caused poor reproducibility and unreliable estimations, B. L. Clarke and H. W. Hermance¹ designed a capillary burette (Fig. 43) to obviate this. The reagent

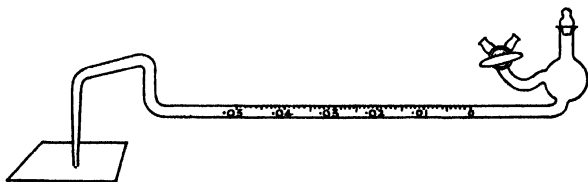


FIG. 43. Capillary Burette.

paper, placed on a small table provided with a central opening, was brought into contact with the tip of the burette containing the test solution. By a suitable mechanism the burette was so inclined that the rate of flow was less than the rate of the reaction. H. Yagoda² confined reactions to a definite area by embedding in the paper rings of inert, water-repellent material. The part within the ring was treated with an excess of the reagent, a drop of the solution added and the surplus liquid drained off below by means of a mat of absorbent paper.

MINERALOGICAL APPLICATIONS

An early experimenter on systematic application of microchemical colour reactions to minerals was J. A. Watson³, who, in a simple manner, applied a series of 33 tests to the detection of 37 elements. Minerals were fused with sodium carbonate and sodium peroxide if required, in a loop of platinum wire. An aqueous extract of the fused bead was made on a watch glass and the solution separated by means of the micro-filter (Fig. 41); the residue was dissolved in hydrochloric acid. A succession of tests was applied to small portions of each solution, allowance being made for interfering effects. This scheme, with little modification, was used by P. W. West and L. Smith⁴ in building a portable drop reaction kit for field and

¹ *Ind. Eng. Chem. (Anal.)*, 9, 1937, p. 292.

² *Ind. Eng. Chem. (Anal.)*, 9, 1937, p. 79; *Mikrochem.*, 24, 1938, p. 117.

³ *Miner. Mag.*, 24, 1935, p. 21.

⁴ *Journ. Chem. Ed.*, 17, 1940, p. 139.

laboratory use, and was afterwards more thoroughly examined for potentially interfering effects¹. The scheme does not include certain important elements for which at the time no suitable reactions were found, nor does it consider the possible interference of these omitted elements on the tests prescribed for the others. Although no doubt suitable for the detection of reasonably pure minerals, the methods are not generally adequate for the detection of minor constituents of mixtures. E. H. Davison² has described similar direct tests for the rapid detection of various elements in grains of minerals.

Recent tests of great sensitivity, applied to minerals, are based on the observation of fluorescence in ultra-violet light. F. Feigl³ tested for tin in cassiterite, stannite, etc., and a columbite containing 0.2% of stannic oxide. A few mg. were dissolved in sulphuric acid and iodide was added to form stannic iodide, which was separated from certain interfering elements by means of benzene containing some iodine. A drop of the extract was appropriately tested with morin on filter paper, tin giving a fluorescent spot. A sensitive test for beryllium with morin, in which many interfering elements were masked with ethylenediaminetetra-acetate, was likewise used for 1 to 2 mg. amounts of minerals that were sintered with ammonium fluoride or fused with sodium bisulphate⁴. A widely applicable fluorescent bead test for uranium⁵ depends on fusion of a tiny grain of mineral with a large excess of sodium fluoride.

An interesting application of many novel reactions now used in inorganic analysis was made by D. Williams and F. M. Nakhla⁶ in the chromatographic contact print method of examining metallic minerals, which serves mainly to determine the constituent elements of opaque metallic minerals in polished sections and discrete grains. In the simple contact print method, gelatine-coated paper, impregnated with a selective attacking reagent, was pressed against a flat, polished surface of the specimen, so that metal ions from the mineral were transferred to the paper. The paper was afterwards developed by a reaction designed to detect only the element sought, in the form of a coloured print showing the distribution of that element throughout the area of the polished section. In the electrographic method, which was applied to conducting specimens, passage of an electric current expedited transfer of metal ions to the paper, on which appropriate tests were then made. Mineral

¹ *Ind. Eng. Chem. (Anal.)*, 13, 1941, p. 271.

² *Field Tests for Minerals*, 2nd ed., (Chapman and Hall, London), 1940.

³ *Mikrochim. Acta*, 1954, p. 93.

⁴ F. Feigl, *Spot Tests in Inorganic Analysis*, translated by R. E. Oesper, (Elsevier, Amsterdam), 1958, p. 458.

⁵ M. A. Northup, *Ind. Eng. Chem. (Anal.)*, 17, 1945, p. 664.

⁶ *Trans. Inst. Min. and Metall.*, 60, 1950-51, p. 257.

grains briquetted on conducting mounts were investigated, and contact prints were also obtained by spraying metallic mineral grains on to gelatine-coated paper, impregnated with suitable reagents.

SEMI-QUANTITATIVE TESTS

In 'Compilation of Field Methods used in Geochemical Prospecting by the U.S. Geological Survey'¹, are included two procedures of general interest, namely, the chromographic method, which is related to H. Yagoda's² confined spot test technique, and the solvent extraction procedure, whereby a coloured organo-metallic complex is extracted into a non-polar organic solvent for visual estimation by colorimetry.

In making quantitative spot tests with large volumes of solution, B. L. Clarke and H. W. Hermance³ caused the test solution to flow through a restricted area of a reagent-treated paper held between two tightly compressed flanges. The chromograph⁴ is based on the same principle, but is for small volumes of solution. It confines areas of 6 mm. diameter on a strip of reagent paper fed through the apparatus and automatically controls rate of flow through the confined spot. Reagent-impregnated papers may be used, or precipitates may be formed in solution and collected. Comparisons are effected with similarly prepared standards. Mixed precipitates collected on the discs may be examined for their components. The method was applied to detection of nickel, later to cobalt in soils and rocks⁵, in 0.2 ml. aliquots of solutions corresponding to 2 to 4 mg. of sample. The precipitants were dimethylglyoxime for nickel, dithio-oxamide for copper and 2-nitroso-1-naphthol for cobalt; the minimum amounts of metal detected were 0.28, 0.04 and 0.02 $\mu\text{g.}$, respectively. Estimations were accurate to about 40 per cent.

In solvent extraction procedures, one of the most important reagents for detection of heavy metals is diphenylthiocarbazone, which dissolves in chloroform or carbon tetrachloride to give a green solution and forms with many metal ions similarly soluble, yellow, red or violet complexes. By suitable control of the conditions of the reaction, with the aid of buffering and masking agents, tests have been worked out for numerous metals. For estimations, a

¹ H. W. Lakin, H. Almond and F. N. Ward, *U.S. Geol. Surv. Circ.*, **161**, 1952.

² *loc. cit.*

³ Paper as a Medium for Analytical Reactions, *Ind. Eng. Chem. (Anal.)*, **10**, 1938, p. 591.

⁴ R. E. Stevens and H. W. Lakin, The Chromograph, A New Analytical Tool for Laboratory and Field Use, *U.S. Geol. Surv. Circ.*, **63**, 1949.

⁵ H. Almond and H. Bloom, *U.S. Geol. Surv. Circ.*, **125**, 1951.

mixed-colour or a mono-colour method may be used¹. In the former, made at pH 5.0 to 7.5, excess reagent is left in the organic phase and the mixed colour is compared with appropriate standards. In the mono-colour method, ammonia is added to the mixed test in order to withdraw the excess reagent into the aqueous layer and the residual colour in the organic solvent is estimated. L. C. Huff² determined heavy metals (copper, lead and zinc), calculated as zinc, in soils and sediments. For the final tests, he took aliquots of the extracts prepared from the samples, corresponding to 16 mg. of the original material. One $\mu\text{g.}$ of zinc and 4 $\mu\text{g.}$ of lead were detectable.

Semiquantitative tests for molybdenum³ and tungsten⁴ have been based on formation of complex thiocyanates which are extracted by isopropyl ether under very different conditions of acidity. Cobalt has been determined as the 2-nitroso-1-naphthol complex, after extraction with carbon tetrachloride⁵.

PAPER CHROMATOGRAPHY

Within recent years, many normally difficult separations of inorganic species have been accomplished on filter paper by the process of partition chromatography, which depends, probably to a considerable extent, upon differential partition of solutes between an aqueous phase held by the paper as an inert support and a mobile phase in equilibrium with it, which is commonly a partially miscible organic solvent. The relative movements of solutes depend on their partition coefficients with respect to the two phases, and are generally given in terms of R_F values, which are defined as:

$$R = \frac{\text{distance travelled by the solute from the starting-point}}{\text{distance travelled by the solvent from the starting-point}}$$

Under a particular set of conditions, R_F values characteristic of various ionic species are obtained. In small-scale work, narrow strips of Whatman No. 1 (or similar) filter paper may be used, either by the method of descending chromatography (Fig. 44A) or that of ascending chromatography (Fig. 44B). The atmosphere in the jar must be kept saturated with the vapour of the solvent system. The mobile phase is placed in the trough (A), or in a shallow dish at the base of the jar (B). About 5 cm. from the end of the paper strip a very small volume (0.01 ml.) of the mixture to be resolved

¹ L. C. Huff, *Econ. Geol.*, **43**, 1948, p. 675.

² *Econ. Geol.*, **46**, 1951, p. 524.

³ F. N. Ward, *Anal. Chem.*, **23**, 1951, p. 788.

⁴ F. N. Ward, *U.S. Geol. Surv. Circ.*, **119**, 1951.

⁵ H. Almond, *Anal. Chem.*, **25**, 1953, p. 166.

is applied, the paper dried, and the end adjacent to the sample placed in the solvent. The latter then diffuses down or up the paper, separating the components of the mixture in accordance with their R_F values and, when the chromatogram has been developed, bands or spots of the separated elements are located by appropriate means.

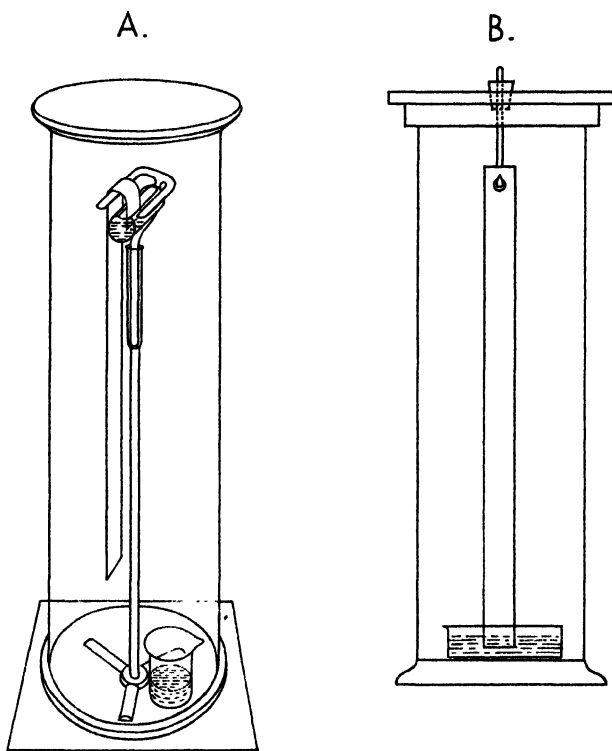


FIG. 44. Arrangements for Paper Chromatography.

A. Descending chromatography.

B. Ascending chromatography.

Since the maximum weight of material for a $\frac{1}{2}$ in. strip is about 0.5 mg., sensitive colour- or fluorescence-producing reactions¹ are invaluable. When the positions of several elements have to be found, non-selective reagents like 8-hydroxyquinoline and diphenylthiocarbazone are preferred. Frequently the further application of

¹ See Chapter XII, p. 442.

characteristic confirmatory reactions is possible. Semiquantitative estimations, based on intensity of colour or fluorescence, and the size of spots or bands, can be made with respect to standards. A full account of these methods and of the many devices used to improve separations is given by F. H. Pollard and J. F. W. McOmie¹. The value of this method in geochemical prospecting for minerals has already been recognised. E. C. Hunt, A. A. North and R. A. Wells² have separated various metals in 0.01 to 0.05 ml. of soil extracts in less than one hour, by the method of ascending chromatography. The accuracy of estimations was about 30%. Chromatographic methods have been developed for copper, cobalt, nickel, niobium, tantalum, lead and uranium and have been used successfully in the field for the first four. Methods are being devised for other metals.

ION EXCHANGE

Ion-exchange techniques make available simple, rapid and effective means of separating some ionic species from each other and from non-electrolytes. Before 1935, natural or synthetic zeolites were used for ion exchange, but since then they have been to a great extent superseded by synthetic resins, which are cross-linked, organic polymer networks with polar functional groups. The resins may be regarded as insoluble acids and bases, the salts of which are also insoluble. Cation exchangers with the properties of strong or weak acids and anion exchangers with those of strong or weak bases are available. For many analytical purposes, strongly acid cation exchangers containing sulphonie acid groups, and strongly basic anion exchangers with quaternary ammonium groups suffice. Well-known examples of these resins, which have capacity for ion exchange over a wide range of pH, are:

Cation exchangers—Dowex 50, Amberlite IR-120 and Zeo-Karb 225.

Anion exchangers—Dowex 1 and 2, Amberlite IRA-400 and De-Acidite FF.

In analytical chemistry, resins of small grain-size are usually appropriately packed in glass columns of simple construction and the desired capacity (Fig. 45). A few tenths of a gram of resin may sometimes suffice for the separation of milligram samples. The resins are commonly prepared in such a form that cation exchangers have hydrogen or ammonium ions available for exchange with

¹ *Chromatographic Methods of Inorganic Analysis*, (Butterworth, London), 1953.

² Application of Paper-chromatographic Methods of Analysis to Geochemical Prospecting, *Analyst*, **80**, 1955, p. 172.

cations in the solution applied to the column, and anion exchangers, hydroxyl or chloride ions, for exchange with anions. The ion-exchange technique is particularly valuable for separating interfering cations from anions and *vice versa*. If the wanted ions are collected on the resin, they are afterwards eluted with a solution containing other ions that displace them. Cations are frequently eluted with a mineral acid and anions with an alkaline solution.

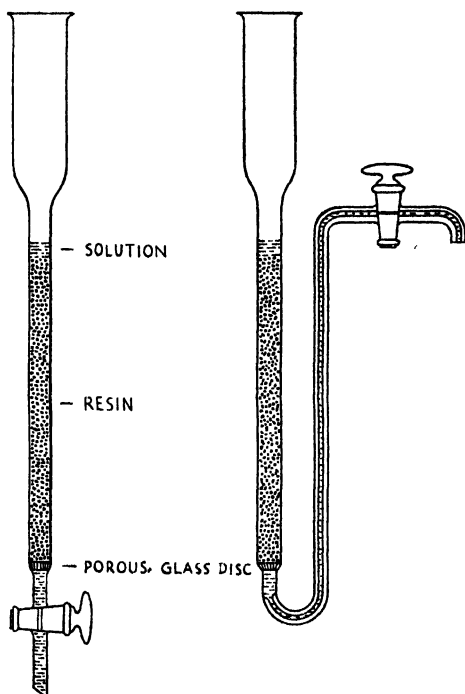


FIG. 45. Columns for Separations by Ion Exchange.

Sometimes a complexing agent is used for the same purpose. Numerous examples of separations important in analysis have been given by O. Samuelson¹. Ion-exchange resins are also of great value for rapidly removing and concentrating electrolytic material from very dilute solutions, such as natural waters.

Separation of two metallic elements from each other may be readily effected when one can be converted into a neutral or an anionic complex, while the other remains cationic. Anions such as

¹ *Ion Exchangers in Analytical Chemistry*, (Wiley, New York), 1953.

cyanide, fluoride, thiocyanate, and water-soluble organic chelating agents (p. 369) have important uses in this connexion.

When ions of the same sign and very similar properties are adsorbed on a resin it may be possible to separate them because of slight difference in their exchange affinities. The elutriant contains another ion of like charge and, as it passes down the column, the previously adsorbed ions tend to separate into bands as the foreign ions displace them. Differential elution may also be effected with a solution of a reagent that forms complexes of slightly varying stability with the different ions.

In mineral analysis for age determination, L. T. Aldritch, J. B. Doak and G. L. Davis¹, with the aid of ion-exchange columns of the resin, Dowex 50, separated concentrates of the alkali and alkaline earth metals from 100 mg. of lepidolite and 1 g. of biotite, with greater ease, higher yield, and less chance of contamination than by conventional chemical procedure. The original materials were treated with hydrofluoric acid which disposed of silica, and perchloric acid which permitted the removal of potassium and rubidium as perchlorates. These metals were adsorbed on the hydrogen form of the resin, after which, elution first with 0.2 N hydrochloric acid and then with 0.4 N acid, led to a hundredfold reduction in the K/Rb ratio. In the filtrate from the alkali perchlorates, about 50 μ g. of strontium had to be concentrated and separated from aluminium, iron, zirconium and calcium in excess of 50 μ g. Glycollic acid was added in order to convert aluminium, iron and zirconium into anionic complexes, from which uncomplexed calcium and strontium were separated by adsorbing them on the ammonium form of the cation exchanger and then washing the column with glycollic acid solution. Calcium was afterwards eluted with 0.5 N, then strontium with 3 N hydrochloric acid.

Excellent reviews on ion exchange have appeared each year, from 1951 to date, in *Annual Review of Physical Chemistry*², and G. H. Osborn³ has prepared a valuable bibliography which includes many references to analytical applications of ion-exchange resins.

QUANTITATIVE METHODS

Practically every type of method applied in chemical analysis, whether purely chemical or physical, can be transposed to a small scale. Chemically, analysis of small quantities of material has been facilitated by introduction of new reagents which, in gravimetric

¹ *Amer. Journ. Sci.*, **251**, 1953, p. 377.

² Edited by G. K. Rollefson and R. E. Powell (*Annual Reviews*, Stanford, California).

³ *Synthetic Ion-Exchangers*, (Chapman and Hall, London), 1955, pp. 89-191.

analysis, provide heavier precipitates for the weighing forms of the elements sought, in titrimetry, perhaps more sensitive indications of equivalence-points, and in photometry, products of characteristic high tinctorial or light-absorbing power. Instrumental methods, such as photometry, polarography and amperometry, are particularly valuable in microchemical analysis.

Whereas the earlier quantitative microchemical analyses of minerals were based to a great extent on classical methods of systematic separation and gravimetric determination of separated elements, recent methods show the same trend as qualitative methods, in that analysis of separate small portions of a complex material, either for single elements or for limited numbers of constituents, is favoured. Titrimetric and instrumental methods often replace gravimetric procedures.

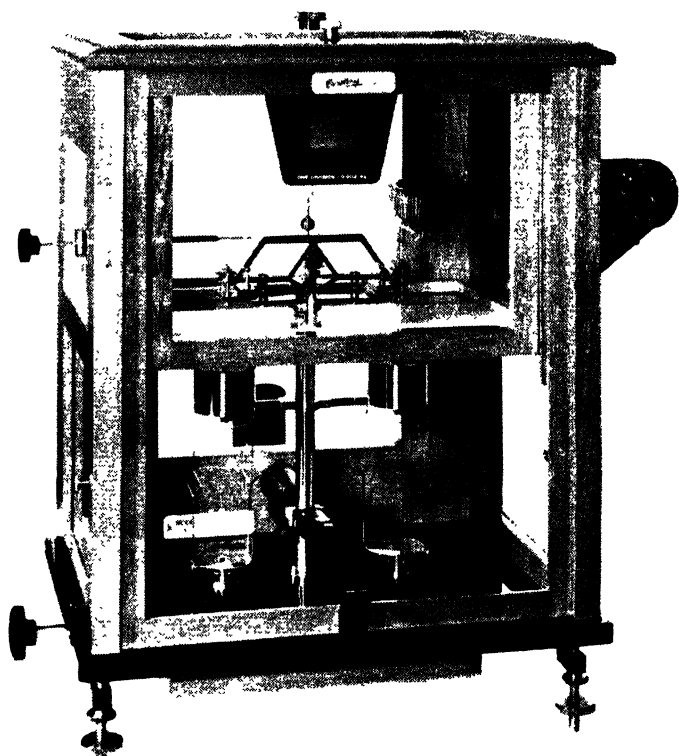
THE MICROCHEMICAL LABORATORY

This is preferably a room of moderate size, with north lighting, in which a microchemical balance can be installed in favourable surroundings, not too far from the working bench, either within the laboratory or in a small adjoining room. There should be accommodation for an ordinary analytical balance, a pH meter-millivoltmeter, a spectrophotometer and perhaps a polarograph and flame photometer. For precise work, a reasonably constant temperature should be maintained with the aid of thermostatically-controlled, tubular electric heaters placed round the room. The humidity of the atmosphere should exceed 50%.

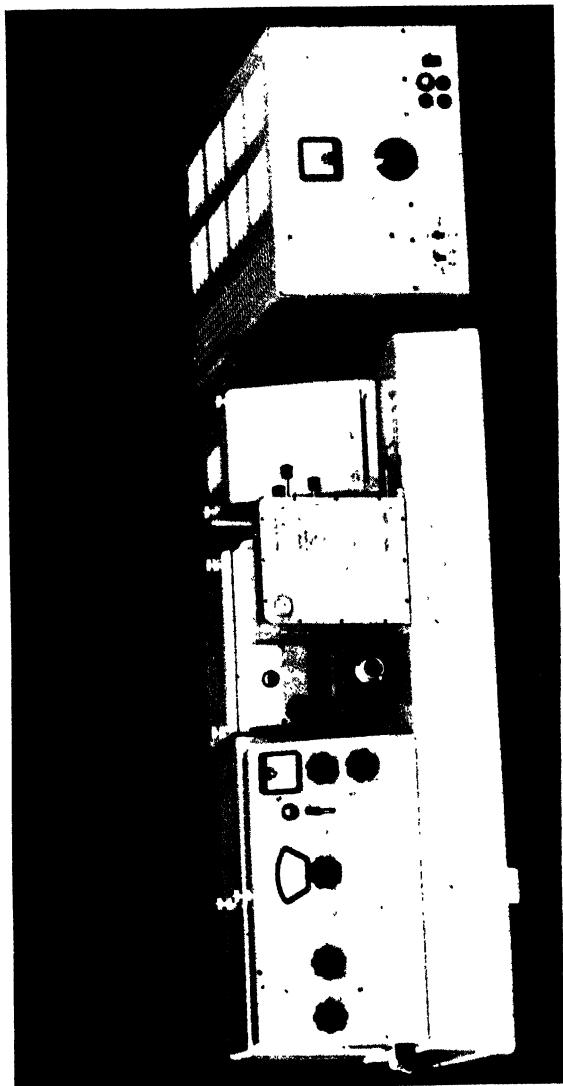
WEIGHING

A microchemical balance, which supports a load of 20 g. and is sensitive to 0.001–0.002 mg., closely resembles an ordinary analytical balance in general construction. It may be free-swinging or air-damped and have projection reading and a multiweight attachment, whereby loading up to 100 mg. may be effected with the balance closed. Recently, a riderless balance (Pl. 10) has become available, in which direct reading of a calibrated scale is substituted for readings of the position of a rider on the beam. As has been stressed by A. Benedetti-Pichler¹, great care is required in setting up and maintaining a microbalance and in effecting weighings with the necessary precision. Weights are little used. Each vessel to be weighed is provided with a tare of approximately the same weight.

¹ *Microtechnique of Inorganic Analysis*, (Chapman and Hall, London), 1942, pp. 174–185; *Mikrochem.*, **34**, 1949, pp. 153, 241 and 298; *Mikrochim. Acta*, 1956, p. 565.



OERTLING MICROCHEMICAL BALANCE.
(Courtesy J. Oertling Ltd. Orpington, Kent.)



HILGER UVISPEK SPECTROPHOTOMETER.
(Courtesy Hilger & Watts Ltd, London, N.W.1.)

Samples, if not weighed directly in the vessels in which analyses have to be carried out, are weighed in small containers. For non-hygroscopic materials a platinum micro-scoop (Fig. 46A), provided with a tare of aluminium wire, is excellent. If a closed container is required, a stoppered, glass weighing-stick, supported on a light-weight metal frame (Fig. 46B), and associated with a tare of glass rod, is appropriate. Additional measures must be taken when appreciably hygroscopic materials are under test¹.

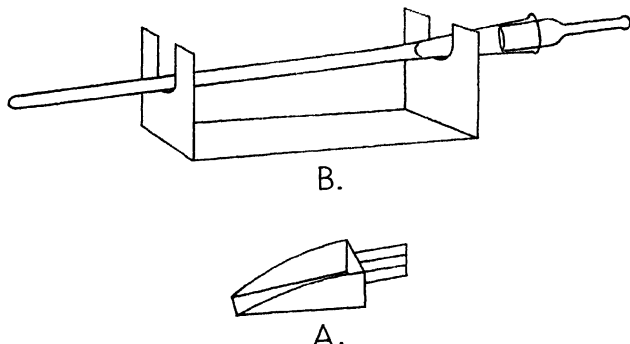


FIG. 46. Micro-Weighing Apparatus.

- A. Micro-scoop.
B. Weighing-stick.

In gravimetric analysis, the tare for glass, porcelain, and metal ware should preferably be a duplicate of the vessel to be weighed. Both should be subjected to the same final heating and cooling before weighing. Cooling is expedited by placing heated ware in suitable cavities drilled in metal blocks. It has been customary to wipe glassware with damp flannel and then with chamois leather, after heating and before weighing, in order to impart to it a reproducible film of moisture. Because trouble may be caused by production of electrostatic charges, it is preferable to wipe it before heating and then, after heating, to place the apparatus in a desiccator containing a saturated solution of calcium nitrate, which allows the glass surface rapidly to assume a settled state.

DISINTEGRATION OF MINERALS

In dissolving samples in liquids in small vessels, metal heating blocks with suitable cavities (*cf.* Fig. 40) are often used in order

¹ R. F. Milton and W. A. Waters, *Methods of Quantitative Micro-Analysis*, 2nd ed., (Arnold, London), 1955, p. 69.

to give an even temperature. When material is dissolved at about 100°C within a micro-beaker, the weight of which has to be kept constant, the beaker is placed in a glass holder resting in a metal support (Fig. 47) on top of a boiling water-bath, so that only steam comes in contact with the surface. Evaporation is accelerated by passage of a gentle current of purified air over the surface of the solution.

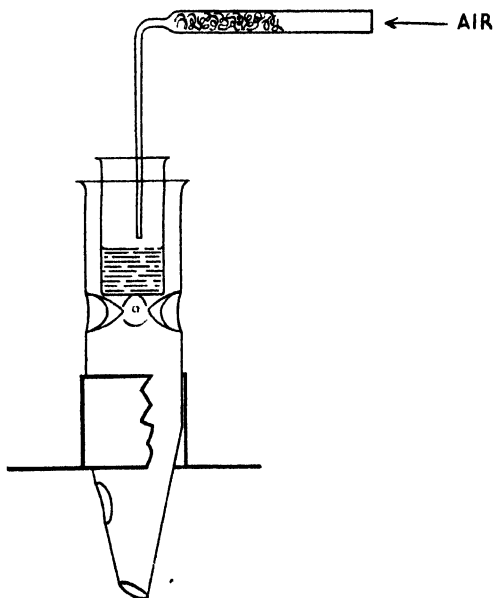


FIG. 47. Beaker Holder.

Fusions with sodium carbonate and potassium bisulphate, etc., and treatments with hydrofluoric acid are usually done in 1 or 4 ml. platinum crucibles. Micro-gas or electric 'Bunsen' burners¹ (infra-red reflex burners) and small electric furnaces are used for heating.

GRAVIMETRIC PROCESSES

In precipitations, gases and liquids are added through fine capillaries. Volatile reagents may be added in an air current, which also acts as a stirrer. Gradual neutralizations with ammonia, as in precipitation of calcium oxalate from an acid solution, or with hydrochloric acid, as in liberation of silicic acid from an aqueous extract

¹ Shandon Scientific Company, 6a, Cromwell Place, London, S.W.7.

of a sodium carbonate melt, are neatly performed in the following manner. The beaker, containing, say, an acid solution, and a crucible with ammonia are placed under cover on one section of a Petri dish resting on a magnetic stirrer hotplate and, within the beaker, a tiny magnetic bar sealed in glass stirs the solution. The hotplate temperature and the concentration of the ammonia solution are adjusted to give the desired rate of neutralization.

FILTRATION

The filter-stick technique is widely used, and much can be done with the simple glass filter designed by F. Emich (Fig. 48A)¹. A tiny spiral

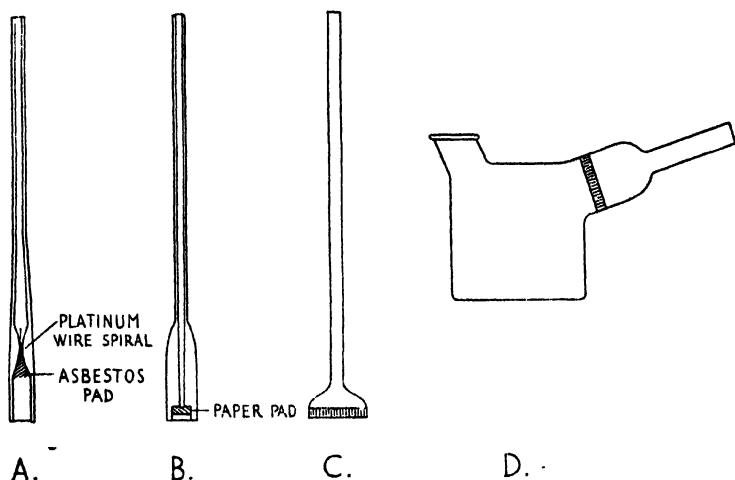


FIG. 48. A, B, C, Filter-sticks. D, Filter-beaker.

of platinum wire placed within the constriction serves as a support for a pad of asbestos, formed by drawing a little asbestos suspension into the bell-shaped part. In filtering, the filter-stick is attached to a capillary tube associated with a suction outfit in which the receiving vessel for the filtrate can be placed (Fig. 49A). A comparable type of filter (Fig. 48B) designed to take a pad of filter paper was used in the micro-analysis of silicates², when the filtering medium had to be destroyed. Sintered glass or porcelain filter-sticks and platinum filter-sticks with a platinum-sponge base (Fig. 48C) have many uses.

¹ *Microchemical Laboratory Manual*, translated by F. Schneider, (Chapman and Hall, London), 1932, p. 69.

² C. C. Miller, *Journ. Chem. Soc.*, 1939, p. 1962.

In the filter-beaker (Fig. 48D), the filter is incorporated in the beaker. When precipitates must be transferred from the vessels in which they are formed, sintered glass filter-tubes or sintered porcelain or platinum Neubauer crucibles may be used (Fig. 49B, C). All can be held in suitable adapters inserted in the stopper of the suction jar.

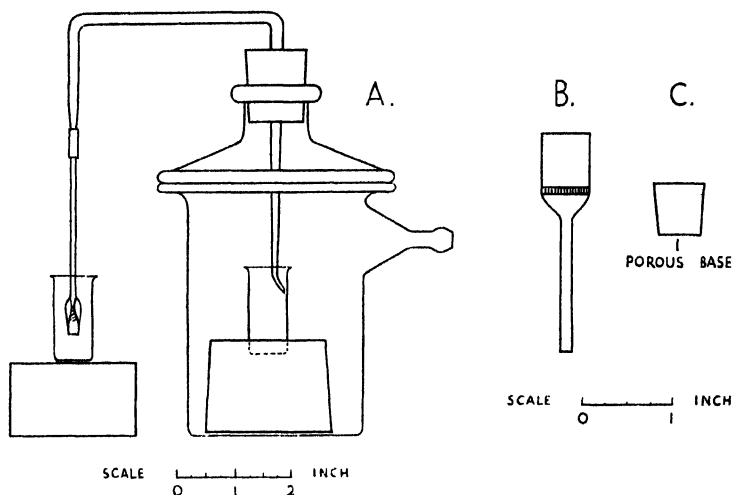


FIG. 49. A. Suction Arrangement.
B. Filter-tube.
C. Neubauer crucible.

New sintered glass and porcelain filters generally lose weight when they are cleaned with acids and it is essential to heat them in hydrochloric acid and to draw acid and water through them until weight constancy is attained.

DRYING AND IGNITION OF PRECIPITATES

The glass assembly (Fig. 50) designed by A. Benedetti-Pichler¹ for beakers and filter-sticks, which is placed within a split metal heating block, is also suitable for filter-tubes and small crucibles. A little oven accommodates the filter-beaker. For high-temperature ignitions, electric furnaces are generally preferred. An electric 'Bunsen' burner (p. 386) with energy regulation is excellent for controlled temperatures below about 800°C.

¹ *Op. cit.*, p. 206.

The filter-stick technique, in experiments relevant to mineral analysis, is fully described by H. V. A. Briscoe and P. F. Holt¹ and by A. Benedetti-Pichler². Experimental technique relating to a much wider range of apparatus is described by F. Hecht and J. Donau³.

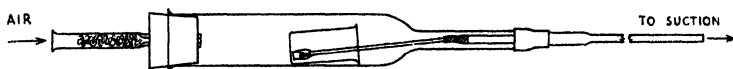


FIG. 50. Heating Block.

TITRIMETRIC PROCESSES

The principles underlying the application, to mg. samples, of titrimetric processes based on the visual observation of a colour change near the equivalence-point, have been outlined by A. Benedetti-Pichler². Micro-methods compare favourably in accuracy with ordinary methods when the concentrations of the reactants and the indicator are kept the same, and the titrant can be added in minute quantities at a time and accurately measured. Small capacity, narrow burettes provided with taps permit accurate measurement, but are inadequate for control of flow-rate. Indiscriminate dilution of the titrant, for improving the accuracy in direct titrations, is not permissible, because displacement of the equilibrium of the reaction may cause the observed end-point to be too far removed from the equivalence-point. Slight over-titration can sometimes be corrected for by back-titration with a very dilute solution of an appropriate reagent. Where direct titration is essential, a tapless burette in a very simple assembly (Fig. 51)⁴ will give the required accuracy of control. The burette, which may be of any desired capacity, may be constructed from narrow precision-bore tubing, to which a thermometer scale is attached, or from a micro-burette (e.g., 1 or 2 ml., subdivided in 0.01 ml.) to which a jet would normally be attached by means of rubber tubing⁵. It has a fine capillary tip, adjusted so that in use a quantity of liquid representing less than one-tenth of a scale division can be added, and is connected with two pressure-controlling bulbs containing water

¹ *Inorganic Micro-Analysis*, (Arnold, London), 1950.

² *Op. cit.*

³ *Anorganische Mikrogewichtsanalyse*, (Springer, Wien), 1940.

⁴ E. Schilow, *Zeit. angew. Chem.*, **39**, 1926, pp. 232 and 582.

⁵ H. J. Elliott, Ltd., Pontypridd, Glamorganshire, Great Britain.

or a heavier liquid. To fill the burette, the liquid in the bulbs is set at the same level, the tip of the burette placed in the solution, and bulb A lowered. When equilibrium is attained, pressure B equals pressure C. Owing to surface forces, when the burette is removed from the solution, A may be raised slightly without starting discharge. Spontaneous discharge occurs if the tip of the burette is dipped into a solution. In a titration, the tip of the burette is kept above the surface of the solution and A is slowly raised. As the

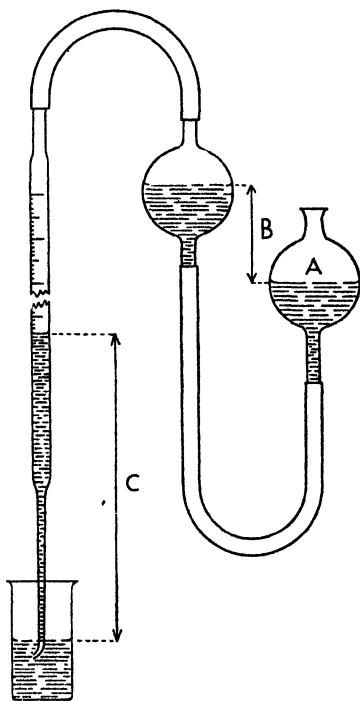


FIG. 51. Micro-Burette Assembly.

equivalence-point is approached, A is fixed in position and, after spontaneous discharge has ceased, minute additions of titrant are made by bringing the solution momentarily into contact at short intervals with the tip of the burette, until the end-point is reached or the burette reading becomes stationary. In the latter case, A is raised a little and the process repeated.

Excellent results are obtainable with very small capacity burettes (0.2 ml.), provided that they are kept clean, filled afresh for every titration, and washed out with water, if the time interval between titrations exceeds 15 minutes. After use, they must be thoroughly rinsed with water, then alcohol, and dried. Constancy of temperature is required. The burettes are calibrated by A. Benedetti-Pichler's method¹.

An 'Agla' micrometer syringe² makes a useful microburette for volumes up to 0.5 ml. Each graduation on the peripheral scale of the micrometer head corresponds to a volume of 0.0002 ml. A glass capillary nozzle is substituted for the hypodermic needle.

Small beakers, flasks and crucibles serve as titration vessels and magnetic stirring is excellent for mixing during titration. Small, standard pattern volumetric flasks serve for most purposes. In measuring aliquots, ordinary 1 ml. bulb pipettes give a precision of 0.001 ml. Weight aliquots are recommended for smaller amounts.

APPLICATIONS OF GRAVIMETRIC AND TITRIMETRIC METHODS IN MINERAL ANALYSIS

H. Thurnwald and A. Benedetti-Pichler³, utilizing F. Emich's filter-stick method, analysed a 3.5 mg. sample of kolbeckite for silicate, phosphate, aluminium, beryllium, calcium and iron. All except the last were determined gravimetrically. 8-Hydroxyquinoline was used for the precipitation of aluminium and iron, and iron was afterwards determined titrimetrically with a solution of potassium dichromate, in conjunction with an oxidation-reduction indicator. In a chemical investigation of dusts known to cause silicosis, J. W. Matthews⁴ analysed 5 to 10 mg. samples for 5 to 7 constituents, among which silica was determined by classical procedure. Sodium and potassium were determined by a simplified Berzelius method.

An excellent review of the results of mineral analyses made up to 1937 has been given by F. Hecht⁵ who, with collaborators, has contributed so much to this field. At that time his work was essentially classical gravimetric, but 8-hydroxyquinoline, cupferron and picrolonic acid were used as precipitants. Time-consuming destruction of organic matter was frequently necessary. Complete analyses of thorianites, pitchblendes, uraninites, monazites, allanites, etc. were made. Analyses of three volcanic glasses⁶ were particularly

¹ *Op. cit.*, p. 258.

² Burroughs Wellcome and Co., London.

³ *Mikrochem.*, 11, 1932, p. 100.

⁴ *Analyst*, 63, 1938, p. 467.

⁵ *Mikrochim. Acta*, 2, 1937, p. 120.

⁶ *Mikrochim. Acta*, 2, 1937, p. 188.

interesting. In general, sample weights were 10 to 20 mg. for each determination or set of determinations. Numerous analyses were also done on one gram samples from which minor components, especially lead, thorium and uranium, were separated and determined by microchemical procedure. There are few references in the review to titrimetric procedures, but several to colorimetric methods. F. Hecht's methods of that period are described in detail in his text-book¹, and it is to be expected that additional new methods will appear in a forthcoming series of books².

Much work has been done by I. P. Alimarin and his associates³ on the quantitative micro-analyses of minerals, ores and rocks. Their work, as deduced from abstracts, includes the application of modern titrimetric and colorimetric procedures to the determination of iron (II and III), chromium, vanadium, titanium, phosphorus and sulphur in 5 to 30 mg. samples, and the gravimetric determination of alkali metals and combined water. A.-G. Hybbinette's⁴ micro-analysis of a sphalerite for 13 constituents was mainly gravimetric. M. Hey⁵ determined ferrous oxide in resistant silicates by modifying Rowledge's method to suit 10 mg. samples.

C. C. Miller⁶ outlined briefly methods for determining zinc in zinc blendes, manganese dioxide in pyrolusites, and various constituents of silicate rocks. More recently, she and R. A. Chalmers⁷ evolved a new method for silica, based on the precipitation of silicic acid from a 3 mg. sample of rock as dimethylquinoline silicomolybdate. Quantitative deposition was obtained in a single step and the separated precipitate was converted into silicomolybdic anhydride by heating it at 550°C. In a method for the direct determination of alumina⁸ in 5 mg. of rock, organic reagents and solvent extraction of organometallic complexes were utilized for isolating aluminium, which was finally converted into aluminium 8-hydroxyquinolate. No high-temperature ignitions were required. In the same sample other elements may be determined. A microreductor containing silver was used in a rapid titrimetric determination of total iron in 5 mg. quantities of silicates⁹. This method was employed by E. A.

¹ *Op. cit.*

² *Handbuch der mikrochemischen Methoden*, edited by F. Hecht and M. K. Zacherl, (Springer, Wien).

³ *Chem. Abs.*, **34**, 1940, p. 7214; **35**, 1941, pp. 1354, 2815 and 7316; **39**, 1945, p. 4018; **40**, 1946, pp. 1422 and 1423; **41**, 1947, p. 3710; **44**, 1950, p. 3404.

⁴ *Ind. Eng. Chem. (Anal.)*, **17**, 1945, p. 654.

⁵ *Mineral. Mag.*, **26**, 1941, p. 116.

⁶ *Quantitative Inorganic Microanalysis for University Students*, *Chem. and Ind.*, 1946, p. 26.

⁷ *Analyst*, **78**, 1953, p. 24.

⁸ C. C. Miller and R. A. Chalmers, *Analyst*, **78**, 1953, p. 686.

⁹ —, *Analyst*, **77**, 1952, p. 2.

Vincent¹ in the analysis of 15 to 20 mg. samples of magnetites and ilmenites. R. A. Chalmers², in an examination of 13 mg. of veachite, determined each of the three main constituents in duplicate, strontium and boric oxide titrimetrically, and water gravimetrically, and thus provided evidence confirming that the composition was $3\text{SrO} \cdot 3\text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and not $3(\text{Sr}, \text{Ca})\text{O} \cdot 8\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

PHOTOMETRIC METHODS

Those most important in quantitative micro-analyses are spectrophotometry, fluorimetry, and flame photometry. The first depends on the conversion of the substance to be determined into a coloured substance or one absorbing ultra-violet radiation; the second, on the formation of a fluorescent compound; and the third, on emission of characteristic radiation by the substance in a hot flame.

In spectrophotometry, radiation of appropriate wavelength is passed through a solution of the substance to be determined and the amount absorbed or transmitted is measured photo-electrically. With reference to a calibration curve showing relationship between concentration and absorbance, the concentration of the substance to be determined is found. Substances show differential absorption of radiation of different wavelengths, and for maximum sensitivity in determination the spectral band selected should normally include the wavelength at which greatest absorption occurs. In filter photometers, in which a continuous light source is available, selection is made by means of a set of different coloured filters, each of which may cover a range of wavelength of 30 to 50 millimicrons ($\text{m}\mu$). In the spectrophotometer proper, a monochromator provides for selection of the desired spectral band which, in an inexpensive instrument, covering a range of 400 to 700 $\text{m}\mu$, may be about 35 $\text{m}\mu$ wide and, in an instrument with a quartz optical system (Pl. 20) and a spectral distribution extending from 200 to 1000 $\text{m}\mu$, a few $\text{m}\mu$ wide. So sensitive are the measuring devices in the best instruments, that volumes as small as 0.05 ml. have been dealt with. Commonly, cells of 10 mm. length and a capacity of a few ml. are used.

Fluorimetric methods (Chapter XII), because of their great sensitivity, are essentially microchemical. Usually a solution of the substance to be determined is exposed to filtered ultra-violet radiation of selected wavelength, and the intensity of the emitted light is measured in the direction at right angles to the path of the incident beam. The concentration, which must be below that at

¹ E. A. Vincent and R. Phillips, *Geochim. et Cosmochim. Acta*, 6, 1954, p. 1.

² F. H. Stewart, R. A. Chalmers and R. Phillips, *Miner. Mag.*, 30, 1954, p. 389.

which self-quenching occurs, is determined with respect to a calibration curve. Fluorimeter attachments are available for quartz spectrophotometers and certain filter photometers.

When reactions involving formation of strongly-coloured or fluorescent complexes are used in conjunction with solvent extraction separations and sensitive measuring instruments, these constitute a powerful means of extending the range of application of microchemical methods. One of the most important general sources of information on these methods is E. B. Sandell's book on *Colorimetric Determination of Traces of Metals*¹. Frequently, methods are prescribed for the determination of 1 to 10 p.p.m. of elements, including rarer metals, in 0.25 to 1 g. of silicate rocks, and it should be easy to arrange for determination of larger amounts in 1 to 10 mg. samples.

Determination of elements separated by paper strip chromatography involves microchemical methods. Attempts to evaluate their coloured complexes on the strips by spectrophotometry have been described by H. C. Ehrmantraut and A. Weinstock² and by H. Campbell and J. A. Smith³. More frequently, the substances are removed from the strips by appropriate elution, or the parts of the paper containing them are ashed and the residues collected. Spectrophotometric methods of determination are then often applied (Pl. 11).

An important application of the spectrophotometer is to the determination of equivalence-points in titrations where, at a given wavelength, a marked change in absorbance occurs at the equivalence-point⁴. An indicator may or may not be needed and operation in the ultraviolet region of the spectrum may be successful with some colourless systems. The methods are applicable to low concentrations of substances in small volumes of solutions, under which conditions visual end-points may be difficult. R. A. Chalmers⁵ determined 30 to 140 $\mu\text{g.}$ of calcium in 3.5 ml. of solution with disodium ethylenediaminetetra-acetate solution as titrant and murexide as indicator. At a wavelength of 610 $\text{m}\mu$, murexide showed appreciable absorption, whereas the calcium-murexide complex did not absorb. Ultimate application to 5 mg. samples of silicate rocks is intended.

In flame photometry, an aqueous solution is sprayed into a flame by means of an atomiser operated at constant air pressure. The characteristic spectrum lines emitted may be isolated by means of

¹ 3rd ed., (Interscience, New York), 1959.

² *Biochim. et Biophys. Acta*, 15, 1954, p. 589.

³ *Chem. and Ind.*, 1953, p. 342.

⁴ A. L. Underwood, Photometric Titrations, *Journ. Chem. Ed.*, 31, 1954, p. 394.

⁵ *Analyst*, 79, 1954, p. 519.

a spectrophotometer or with the aid of filters, and the intensity of the radiation measured photoelectrically. With reference to a calibration curve relating concentration and instrument reading, the required concentration is determined. A flame attachment is available for certain quartz spectrophotometers. At the temperature of a coal gas flame an appreciable amount of radiation is emitted, chiefly by the alkali and alkaline earth metals, whose spectra are simple and capable of resolution by filters. Inexpensive flame photometers that operate under these conditions are available for determination of sodium, potassium, lithium and calcium. Determinations are preferably made at high dilution in order to minimize certain interferences and, since full-scale deflection of the instrument may be shown by about 5, 10, 20 and 40 p.p.m., respectively, of the above elements, and only a few ml. of solution are required, it is evident that the method is suitable for microchemical analyses.

SOME APPLICATIONS OF PHOTOMETRIC METHODS

Mention has already been made (p. 392) of application of colorimetric methods in microchemical mineral analysis by I. P. Alimarin and his co-workers. A.-G. Hybbinette used colorimetric methods for determination of bismuth and manganese in sphalerite (see p. 392). R. A. Chalmers¹ determined 0.02 to 3% of phosphoric oxide in 5 mg. of silicate rocks, in a very simple procedure in which the interference of silicic acid was suppressed during the formation of the blue reduction product of phosphomolybdic acid. In the semimicro-analyses of ilmenites and magnetites, E. A. Vincent² determined 9 of 15 constituents photometrically. The strong absorption of ultra-violet radiation by numerous substances, particularly at low concentrations, is being increasingly made use of in analysis. In the determination of tantalum in two tantaloniobates and a columbite, J. I. Dinnin³ formed the pyrogallol complex and measured its absorbance at a wavelength of 325 m μ . The analysis of the columbite involved no separations, and sensitivity and reproducibility of the method were better than in gravimetric experiments. Although 0.05 to 1 g. of mineral was used, the solution for the final test contained only 0.002% of tantalic oxide, indicating that a micro-sample could have been used.

The great sensitivity of fluorimetric procedures is shown in the work of F. S. Grimaldi, F. N. Ward and R. K. Fuyat⁴, who determined 0.001 to 0.1% of uranium in 3 mg. samples of phosphate rocks, shales and carnotite-bearing deposits. The sample was fused

¹ *Analyst*, **78**, 1953, p. 32.

² *Loc. cit.*

³ *Anal. Chem.*, **25**, 1953, p. 1803.

⁴ *U.S. Geol. Surv. Bull.*, 1006, 1954, p. 69.

with 3 g. of a fluoride-carbonate flux and a phosphor in disc-form prepared, the reflected fluorescence from which was measured photometrically.

A good deal of attention has been paid to the determination of alkali metals and calcium in minerals by flame photometry. Although micro-samples have not been used, small fractions of the prepared solutions required for the final test indicate that large samples are not needed. F. M. Biffen¹ effected decomposition of refractories by the Lawrence-Smith procedure and determined sodium and potassium directly in the suitably prepared aqueous extract of the sintered mass, in which calcium was the only other element present in significant amount. To the standard alkali chloride solutions he added calcium chloride, the amount of which did not require to be rigorously controlled. G. H. Osborn and H. Johns² decomposed an assortment of minerals by means of hydrofluoric and sulphuric acids and described a method for obviating interference of other elements. According to them, a 5 mg. sample would suffice for determination of 0.5% of soda.

In the rapid methods of analysis of silicate rocks, devised by L. Shapiro and W. W. Brannock³, silica, alumina, ferric oxide, titania, phosphoric oxide and manganese oxide were determined spectrophotometrically, soda and potash by flame photometry, and lime and magnesia titrimetrically with disodium ethylenediaminetetraacetate. As 1.1 or 0.45 g. of sample was used and volumes were large, excessive care in measuring was unnecessary. The scale of operations could easily be reduced, but extra time would have to be allowed for the greater care required in handling small volumes.

ELECTROCHEMICAL METHODS

A valuable review of these methods is given by J. T. Stock in *Methods of Quantitative Micro-analysis*⁴, pp. 421-520. See also Chapter X, p. 399.

POTENTIOMETRY

Potentiometric titrations⁵ are frequently of value in small-scale work. Since the end-point is found graphically from a plot of potential against the volume of titrant, which is added until a small excess is present, a micro-burette with a tap may be used. The end-point occurs where the rate of change of potential is a maximum.

¹ *Anal. Chem.*, **22**, 1950, p. 1014.

² *Analyst.* **76**, 1951, p. 410.

³ *U.S. Geol. Surv. Circ.*, **165**, 1952; *U.S. Geol. Surv. Bull.*, **1036-C**, 1956.

⁴ R. F. Milton and W. A. Waters, 2nd ed., (Arnold, London), 1955.

⁵ I. M. Kolthoff and H. N. Furman, *Potentiometric Titrations*, (Chapman and Hall, London), 1931.

A pH meter, incorporating a thermionic valve, is used as a potentiometer, and no special titration cells are required for volumes of solution exceeding 1 ml. For neutralizations, a miniature glass electrode is inserted in the solution and a calomel electrode is connected via a salt bridge. In oxidation-reduction titrations, very dilute solutions may often be used; a platinum wire replaces the glass electrode. See also Chapter X, p. 409.

POLAROGRAPHY¹

Polarographic methods of analysis are essentially microchemical, since they are applicable to small volumes of electrolysable materials at low concentrations (10^{-2} to 10^{-6} molar). They are based on interpretation of current-voltage curves which are obtained when a gradually increasing potential is applied to the solution in a cell, in which one electrode is composed of mercury falling in tiny drops from a capillary, and the other may be a quiet pool of mercury. Records may be obtained manually, or automatically by photography or a recording pen. At first, as voltage is gradually increased, a very small current flows through the solution, but when the decomposition potential of an ion is reached, electrolysis begins and the curve rises steeply until the diffusion current, as it is called, reaches a constant limiting value (Chapter X, p. 410). The potential of the dropping electrode, when the current has attained one half of the limiting value (the half-wave potential) is characteristic of a particular ion in the prevailing medium, and the height of the wave is frequently proportional to its concentration. When their half-wave potentials are sufficiently far apart and their concentrations are similar, 3 or 4 substances may sometimes be determined at the same time. Polarographic methods are as sensitive as spectrophotometric methods and are often used for the determination of substances removed from paper strip chromatograms.

E. Claffy² refers to the use of the polarograph for determining traces of lead, manganese, thallium and tin in calcite and halite, traces of iodate in Chili-saltpetre, molybdenum in its ores and titanium in titanium minerals. That author lists possible applications in geochemistry. A.-G. Hybbinette determined 0.2% of lead and cadmium in a 5 mg. sample of sphalerite (see p. 392).

AMPEROMETRIC TITRATIONS

These are based on polarographic procedure and are most commonly associated with precipitation reactions in which at least one reactant is electrolysable. A constant voltage is applied, at which maximum

¹ I. M. Kolthoff and J. J. Lingane, *Polarography*, Vols. I and II, (Interscience, New York), 1952.

² *Amer. Journ. Sci.*, **247**, 1949, p. 187.

diffusion current of the electrolysable substance or substances will be obtained. When an electroreducible substance is titrated with an inert titrant, a plot of current against volume of titrant tends towards the form shown in Chapter X, Fig. 59. The reverse of this titration is indicated by B and interaction of two electroreducible substances by C. Since dilution of the solution during titration results in deviation from linearity in the two parts of the curves, and slight solubility of the precipitate causes a rounding at the equivalence-point, the titrant is made as concentrated as is practicable, and only a few points are plotted, some distance before and after the equivalence-point. The intersection of the two straight lines drawn through the points is the location of the equivalence-point. The titration cell may be the same as that used in polarography, but with provision for insertion of the tip of a burette. The dropping mercury electrode may be replaced by a rotating platinum micro-electrode, which is satisfactory at applied potentials for which the other electrode is unsuitable. An interesting account of the application of amperometric titration to micro-analysis is given by T. D. Parks¹.

MICROCHEMICAL COMBUSTION METHODS^{2, 3}

Occasional use of these may be required. E. Dittler and R. Reissner⁴ determined carbon in 1 to 2 mg. of diamond powder by using a micro-combustion train. I. P. Alimarin⁵, in determining water in minerals, carried out a combustion on similar lines to that for hydrogen. W. Reich-Rohrwig's⁶ apparatus for the determination of carbon dioxide in 10 to 30 mg. samples of various carbonate minerals contained many components of a classical carbon-hydrogen combustion outfit.

For those desirous of obtaining up-to-date information on all aspects of microchemical methods and on analytical and instrumental procedures that might be of value in connexion with them, reference should be made to the annual reviews that have appeared since January, 1949, in *Analytical Chemistry*. An important treatise, part of which is still in course of preparation, is *Traité de Micro-Analyse Minérale, Qualitative et Quantitative*, C. Duval (Presses Scientifiques Internationales, Paris).

¹ *Anal. Chim. Acta*, **6**, 1952, p. 553.

² F. Pregl, *Quantitative Organic Microanalysis*, revised by J. Grant, (Churchill, London), 1951.

³ S. J. Clark, *Quantitative Methods of Organic Microanalysis*, (Butterworth, London), 1956.

⁴ See F. Hecht's review, *Mikrochim. Acta*, **2**, 1937, p. 146.

⁵ *Chem. Abs.*, **35**, 1941, p. 1354.

⁶ *Zeit. anal. Chem.*, **95**, 1933, p. 315.

CHAPTER X

ELECTROCHEMICAL METHODS OF MINERAL ANALYSIS

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Principles—Theoretical Basis of Electrochemical Analysis—Electrolysis—Electrode Potential—Conductance of Solutions—Electrodeposition Methods—Gravimetric Determinations—Internal Electrolysis—Coulometric Methods—Conductimetric Methods—Applications—Potentiometric Methods—The Polarographic Method and Its Development—Amperometric Titrations.

PRINCIPLES

ELECTROCHEMICAL methods of analysis are those in which either an electric current is employed to effect the analytical process or a measurement of some electrical property of the system under investigation is used to give the analytical result. The methods may be grouped into a number of types as follows: electrodeposition methods, coulometric methods, conductimetric methods, potentiometric methods, polarographic methods and amperometric methods. Although these methods have been employed in mineral analysis, their usefulness and convenience merits a more frequent application in this field. The principles of the methods are discussed fully in a number of excellent textbooks^{1, 2, 3, 4, 5} and are based upon the fundamental laws of electrochemistry. A brief review of these principles follows.

¹ S. Glasstone, *The Electrochemistry of Solutions*, (Methuen, London), 1937.

² H. J. S. Sand, *Electrochemistry and Electrochemical Analysis*, 3 Vols., (Blackie, London), 1941.

³ H. Diehl, *Electrochemical Analysis with Graded Potential Control*, (Smith, Ohio), 1948.

⁴ J. Lingane, *Electroanalytical Chemistry*, (Interscience, New York), 1953.

⁵ P. Delahay, *New Instrumental Methods in Electro-Chemistry*, (Interscience, New York), 1954.

THEORETICAL BASIS OF ELECTROCHEMICAL ANALYSIS

(a) *Electrolysis.* The immersion of electrodes of conducting material into an electrolyte solution causes migration of the ions under the potential difference. The current carried through the solution is caused by the migration of cations (positively charged) to the cathode and anions (negatively charged) to the anode. In order that a steady current may flow, the applied voltage must be greater than a certain minimum value determined by the nature of the electrodes and the solution into which they dip.

When the potential difference between the electrode and solution is sufficient to cause a current to flow, the amount of electrochemical action (deposition of a metal, evolution of oxygen, etc.) is governed by the laws of electrolysis enunciated by Faraday. These are (i) 'The amount of chemical decomposition, or the amount of a substance deposited on an electrode is proportional to the amount of electricity passed through the electrolyte' and (ii) 'The amounts of different substances liberated at an electrode are proportional to their chemical equivalents'.

These two quantitative laws may be summarized by the equation

$$W = \frac{Iet}{F} \quad . . . (1)$$

where w = mass in grams of the liberated substance,

e = equivalent weight of the liberated substance,

I = current in amperes,

t = time current flows, in seconds,

F = Faraday's constant = 96,500 coulombs.

This quantitative relationship is the basis of the coulometric methods mentioned above.

(b) *Electrode potential.* An electrode of a metal immersed in a solution of its ions assumes a steady potential with regard to the solution quantitatively expressed by the Nernst equation as follows:

$$E = E_0 + \frac{RT}{zF} \log_e a_M \quad . . . (2)$$

where E_0 = the standard electrode potential of the metal in volts with respect to the normal hydrogen electrode,

E = potential in volts between the metal and the solution,

z = the valency of the metal ions,

a_M = the activity of the metal ions in solution,

R = the gas constant,

T = absolute temperature,

F = Faraday's constant.

A more practical form of this equation is

$$E = E_0 + \frac{0.0001982}{z} T \log_{10} a \quad \dots (3)$$

or for a univalent ion at room temperature (18°C)

$$E = E_0 + 0.058 \log_{10} a \quad \dots (4)$$

Since the activity of a metal ion species is approximately proportional to its concentration C , it may be said that

$$\Delta E \approx K \log_{10} \Delta C$$

at constant temperature. This is the basis of the potentiometric methods of analysis.

The Nernst equation holds accurately only for a metal in reversible equilibrium with its ions. If the electrode is made more negative than the equilibrium value by connecting it to a source of current, the metal ions will migrate to it and deposition will tend to occur. If, on the other hand, the electrode is made more positive, ions will tend to dissolve from it.

Electrodeposition upon other metals than the ionic species in solution will of course not follow these rules, but as soon as a coating of deposit has been effected the potential will be governed by a similar relationship:

$$E_D = E_0 - V + \frac{RT}{zF} \log_e a_M \quad \dots (5)$$

$$\text{or} \quad E_D = E_0 - V + 0.058 \log_{10} a_M \quad \dots (6)$$

for a univalent metal.

Here E_D is the deposition potential, V is the overvoltage for the process and the other symbols have the significance previously defined. E_D is characteristic of the metal being deposited and is dependent upon its activity or concentration. It also changes with the current flowing in a manner illustrated in Fig. 52.

Here it will be seen that a solution containing metal 1 will deposit under all conditions depicted and even if metal 2 is present the latter will not reach its deposition potential.

However, if an attempt is made to deposit metal 1 completely, the last term in equation (6) will have an effect. When the concentration (activity) has been reduced to one-tenth of its original value, the deposition potential will become more negative by 0.058 volt, so that the deposition curve will advance to the right by 0.058 volt for each tenfold decrease in concentration. Thus, if quantitative results are required to one part in a thousand, the final position

of the deposition curve will be as in Fig. 53 and if no deposition of the second metal is to occur, the electrode must not be made more negative than E_{D_2} . The current thus cannot exceed the value marked C for a complete separation of metal 1 from metal 2. These considerations are at the basis of quantitative electrodeposition methods by potential control.

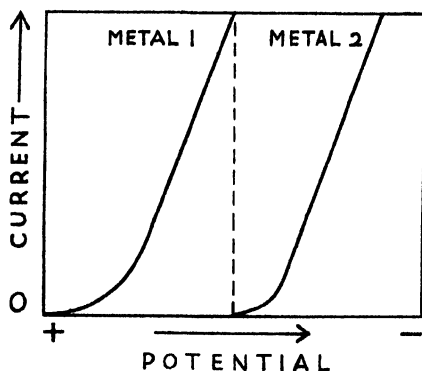


FIG. 52. Current-Potential Curves.

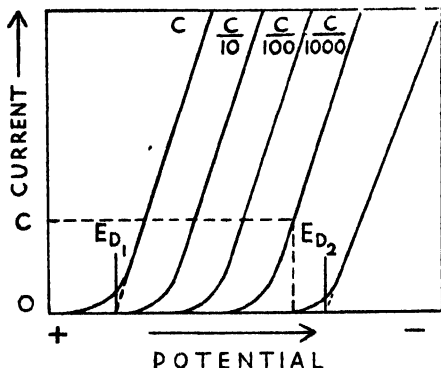


FIG. 53. Conditions for Separation of Metals.

(c) *Conductance of Solutions.* Ohm's law applies generally to electrolytic solutions, but in order to measure the resistance of an electrolyte, it is necessary to avoid the effects of electrolysis (polarization). This is usually done by employing alternating current and a catalytic electrode to minimize polarization. Such methods are also

employed when conductance measurements are made in the processes of analytical techniques.

If Ohm's law is applied to a solution,

$$I = \frac{E}{R} \quad \dots (7)$$

where I = current flowing in amperes,

E = potential difference between the two electrodes,

R = resistance of the electrolyte.

This may be written

$$k = \frac{I}{E} \quad \dots (8)$$

where $k = I/R$ and is called the conductance of the electrolyte.

For a body of electrolyte of known composition and of unit length and cross-section, k has a definite value κ , the specific conductance or conductivity.

Now in an electrolyte the ion migration provides the conductance and since the conducting power of an ion will depend upon the valency, it is useful for comparative purposes to compare equivalent conductances.

The equivalent conductance of an electrolyte Λ is defined by the equation

$$\Lambda = KV \quad \dots (9)$$

where V is the volume containing one gram equivalent. As this volume becomes larger, Λ approaches a limiting value, Λ_∞ which is the greatest value possible and corresponds to the condition in which all ions contribute their maximum effect towards the conductances. The effect of each ion is additive

$$\Lambda_\infty = l_a + l_c \quad \dots (10)$$

where l_a is the ion conductance (or mobility) of the anion and l_c is the ion conductance (or mobility) of the cation.

The ionic conductance of an ion has a characteristic value that may be utilized in conductimetric analysis.

ELECTRODEPOSITION METHODS

These are of most value for determination of the metallic elements. A known amount of the mineral has to be dissolved first and then the solution is analysed by an appropriate technique. The deposit of metal is weighed on the electrode as the element and several metals may be deposited in turn and so determined. Important

advantages of the method are that the metallic deposits are pure, and that the results are independent of atomic weights as the element itself is weighed. The method is applicable to large-scale and small-scale determinations.

MACROGRAVIMETRIC DETERMINATIONS

The principles of the technique originated by Sand¹ are shown in Fig. 54.

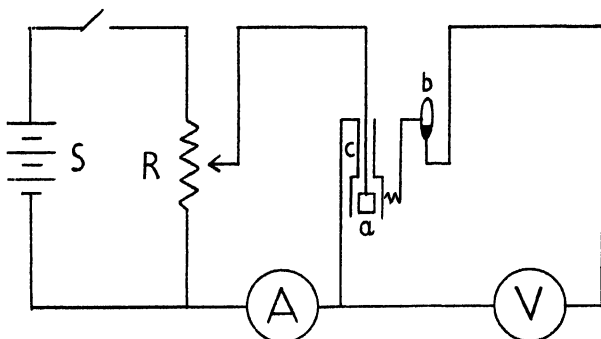


FIG. 54. Apparatus for Potential Controlled Electrolysis.

The source of current S is controlled by the resistance R which allows the applied potential to be selected from all values up to that of the source. The current, measured by the ammeter A , is passed into the electrolytic cell which contains two concentric platinum gauze electrodes, one of which (the anode a), is rotated to stir the electrolyte. Outside the other electrode c an auxiliary electrode b consisting of a standard half cell is placed and the potential between this and the cathode is measured by the valve voltmeter V . Thus the deposition potential is controlled. The sequence of operations is:

1. The cathode is weighed and fitted to the stand.
2. The solution is brought into position.
3. The auxiliary electrode is put in.
4. The stirring anode is started.
5. The temperature is adjusted.
6. The current is switched on and the potential difference raised until deposition potential is attained.

¹ H. J. S. Sand, *Journ. Chem. Soc.*, **91**, 1907, p. 373.

7. The potential difference is kept at this value until the current falls to a low value.
8. The potential difference is raised by 0.05 volt and 7 repeated. This is repeated once more.
9. The container is lowered, the electrodes washed and the washings kept.
10. The cathode is dipped in turn into two separate containers of acetone, dried and weighed.

Other metals may then be determined in the residual liquid and washings.

Automatic control of potential has been devised by Caldwell, Diehl and Parker¹ and by Palmer and Vogel². In these devices the adjustment of the potential controller is effected through a servo-mechanism as the metal separates.

The usual amounts deposited are of the order of several tenths of a gram and are accurate to one part in a thousand.

In some mineral analysis it is convenient to take small particles separated from a sedimentary deposit by hand selection under a binocular microscope and to dissolve these and then deposit by the microchemical method. A great deal has been published on microchemical scale electrodepositions and these techniques have been reviewed³. Sand and Lindsey⁴ first applied the well-established methods of potential control to small scale electrolysis and showed that analytical samples of a few milligrams will serve for a complete analysis. In this method, stirring is effected by a stream of gas bubbles, and the anode-cathode potential difference in the presence of a great excess of anodic depolarizer is used as a means of controlling the deposition. Several metals may be determined in succession⁵, and in this technique the process is similar to the larger-scale method, although the accuracy is somewhat lower.

INTERNAL ELECTROLYSIS

This is a gravimetric method of electrolytic analysis, which employs no external source of current and gives excellent results for traces of metals in the presence of much larger quantities of less noble metals, has especial value in mineral analysis. Although the principles of this method have been known for about a century, the term

¹ C. W. Caldwell, H. Diehl and R. C. Parker, *Ind. Eng. Chem. (Anal.)*, **16**, 1944, p. 532.

² J. F. Palmer and A. I. Vogel, *Analyst*, **78**, 1953, p. 428.

³ A. J. Lindsey, *Analyst*, **73**, 1948, p. 67.

⁴ H. J. S. Sand and A. J. Lindsey, *Analyst*, **60**, 1935, p. 739.

⁵ A. J. Lindsey and E. A. Tucker, *Anal. Chim. Acta*, **11**, 1954, pp. 149 and 260.

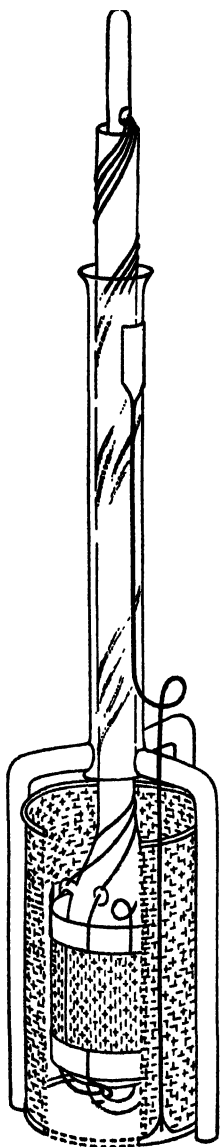


FIG. 55. Electrodes for Gravimetric Determinations.

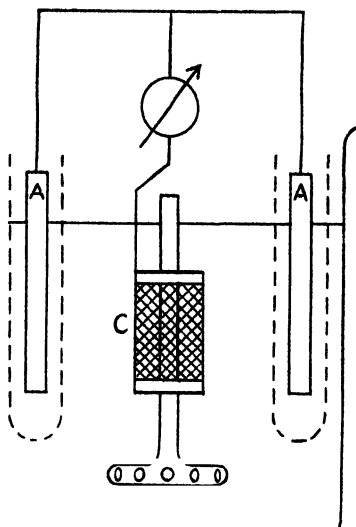


FIG. 56. Principle of Internal Electrolysis.

'Internal Electrolysis' was first employed by Sand^{1, 2} under whose direction much of the early development was carried out.

The method employs a cell in which two compartments are separated by a porous diaphragm (parchment diffusion shell). In one compartment the solution to be analysed is placed together with a stirrer and a weighed platinum gauze electrode. In the other a strong solution of the baser metal present in the first is placed with an electrode of this metal. The two electrodes are connected and a current, generated from the primary cell so formed, deposits the nobler metal traces in the first solution on the cathode, which is weighed again after drying. It is useful

¹ H. J. S. Sand, *Analyst*, **55**, 1930, p. 309.

² H. J. S. Sand, *Electrochemistry and Electrochemical Analysis*, (Blackie, London), II, 1942, p. 108.

to have a milliammeter in series to measure the current flowing, so to indicate the end of the electrolysis. The method has been used in a number of mineral analyses, notably for silver in galena or pyrite¹ and for bismuth and copper in galena² and in the determination of trace impurities in alloys. The method has great utility and should be applied more widely in mineral analysis.

In Fig. 56 the essentials of Sand's apparatus are shown. A cylindrical platinum gauze cathode *C* is held between two anodes, *A*, immersed in a strong solution of the baser metal salt contained in porous diffusion shells. The analytical solution is agitated by means of a centrifugal stirrer concentric with the cathode.

COULOMETRIC METHODS

These methods employ measurement of current for analysis of a mixture and depend upon Faraday's First Law. Generally the reagent to react with the constituent is generated by electrolysis and is measured by the current and time of electrolysis.

Nearly all processes that can be carried out by titration can be effected by coulometry³ and in many cases coulometry will give an accurate method that is not possible with simple volumetric titrations. The most satisfactory type of apparatus is an adjustable constant current source and a timing device. If time-controlled a.c. mains are employed to power the constant current supply the timing device may be incorporated in the unit and, indeed, with small additional complication, the whole outfit may be made automatic. A useful coulometric outfit has been described by Carson³ and applied to the determination of uranium⁴ in milligram amounts.

The method has few limitations. The most important precaution is to ensure that only one or several known constituents react under the conditions of electrolysis. A preliminary separation of constituents by other means may therefore be necessary. The quantities for which the method is employed are in the microchemical range (up to a few milligrams).

Frequently the end point is detected by the potential of an indicator electrode, so that the method is a combination of coulometry and potentiometry.

CONDUCTIMETRIC METHODS

The most important application of conductimetric methods of analysis is in end point determination of titrations. In such methods

¹ E. M. Collin, *Analyst*, **54**, 1929, p. 654.

² *Ibid.*, **55**, 1930, pp. 312 and 68.

³ W. N. Carson, *Anal. Chem.*, **25**, 1953, p. 226.

⁴ *Ibid.*, p. 466.

there is no need to prepare exceptionally pure (conductivity) water or to take great care in standardizing electrical circuits. The essential items of equipment needed are:

1. A source of alternating current which may be the 50-cycle mains current stepped down in voltage to a convenient value by means of a transformer, or a simple valve oscillator such as the cathode coupled double triode oscillator described by Stock¹.

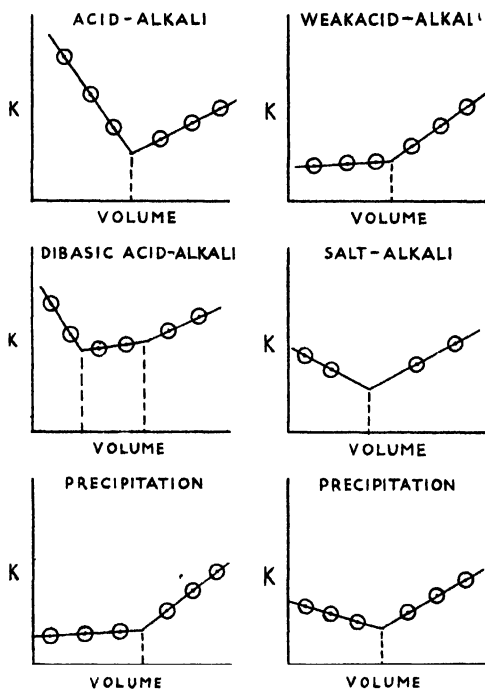


FIG. 57. Typical Titration Curves.

2. A detecting device which can be a rectifier and d.c. galvanometer or a valve amplifier feeding a 'magic eye' tuner-tube.
3. Resistances to make a suitable bridge network and
4. An electrode system to measure the conductance of the solution under test. The most convenient of these are of the immersion type.

A very convenient instrument, embodying all the essential requirements to work with such an electrode-system is marketed by Messrs. Baird and Tatlock Ltd., (London).

¹ J. T. Stock, *Analyst*, 73, 1948, p. 600.

The essential point in applying the method is to observe the inflexion point in the volume-conductance curve during a titration. The method is applicable to most reactions in solution, even in the presence of other ions than those reacting and in the presence of sediments and coloured materials.

A few typical titration curves are shown in Fig. 57.

APPLICATIONS

The methods may be applied on a microchemical scale as well as on more conventional scales. The former are especially useful in mineral analysis. A few examples are, the determination of fluoride in amounts down to 12 μg by titration with aluminium chloride¹, chloride down to 10 μg . with silver nitrate solution², and various metals, in μg . amounts (bismuth, copper, silver, lead and cadmium) titrated with hydrogen sulphide solution³. A useful application to water analysis has been described by Polsky⁴. J. T. Stock describes a number of useful conductimetric cells for this type of work (*loc. cit.*).

POTENTIOMETRIC METHODS⁵

The principles have previously been mentioned (p. 396) and from these it is obvious that the methods fall into two classes.

First, single potential measurements give a measure of concentration (activity) of the constituent required. These methods are of limited application, the most common being the examination of pH or hydrogen ion activity. A number of useful valve voltmeters with appropriate glass electrode systems measuring the pH directly are now available.

Secondly, potential readings may be taken during titrations with the object of indicating the end point. Many of the pH meters are adapted to this use and are provided with an alternative millivolt scale for this purpose. In this method the electrode system responding to the change in ionic activity according to the equations of either Nernst:

$$E = E_0 + \frac{RT}{zF} \log_e a_M$$

or Peters:

$$E = E_0 + \frac{RT}{zF} \log_e \frac{a_{\text{oxidizer}}}{a_{\text{reducer}}}$$

¹ J. Jarms and G. Jander, *Z. Elektrochem.*, **42**, 1936, p. 315.

² G. Jander and H. Immig, *Z. Elektrochem.*, **43**, 1937, p. 211.

³ H. Immig and G. Jander, *ibid.*, p. 207.

⁴ J. W. Polsky, *Anal. Chem.*, **19**, 1947, p. 657.

⁵ See also Chapter IX.

gives a rapid change in e.m.f. at the end point, which is readily recognized by a valve voltmeter or similar instrument. Application of this technique to neutralizations, reductions, oxidations or precipitations of insoluble metal salts gives a range of methods well suited to mineral analysis on a macro- or micro-analytical scale. One advantage is that successive determinations may be made in a single sample of a number of constituents, for example, the determination of iron, vanadium and uranium by permanganate.

The microchemical scale determinations have special attraction in mineral analysis and suitable apparatus has been reviewed and devised by Stock¹. Useful bibliographies have been compiled by Ashcroft² and Furman³.

THE POLAROGRAPHIC METHOD AND ITS DEVELOPMENTS

Polarography is essentially the electrolysis of a dilute solution at a small, and therefore heavily polarized electrode, in the presence of a great excess of an electrolyte which is not decomposed under the conditions employed. The current-voltage curve is plotted either manually or automatically and the curve obtained has the general shape shown in Fig. 58.

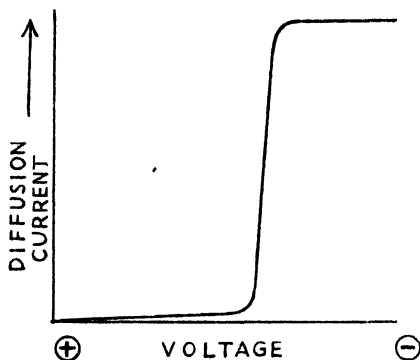


FIG. 58. Diffusion Current Voltage Curve.

Little current flows until the deposition potential of the ionic species being analysed is attained and then the current rises rapidly as described on p. 401. However, since only a small amount of the total electrolyte present is electrolysable, the magnitude of the

¹ J. T. Stock, *Analyst*, **73**, 1948, p. 321.

² E. B. Ashcroft, *Trans. Amer. Electrochem. Soc.*, **48**, 1940, p. 63.

³ N. H. Furman, *Ind. Eng. Chem. Anal.*, **2**, 1930, p. 213; **14**, 1942, p. 367.

possible current is limited and becomes almost constant at a somewhat more negative potential. At this stage, all the cations present are responsible for conveying the current, but only the depositable cations carry it from the electrolyte to the electrode; the upper limit is provided by the maximum rate at which these ions can diffuse through the layer of electrolyte in close proximity to the electrode. The essential process in polarography is therefore ion diffusion and the magnitude of the limiting current is called the diffusion current.

The diffusion is governed by Fick's law, which states that the rate of diffusion is proportional to the concentration gradient and for a thin layer, in which the electrolyte is exhausted at the surface of the electrode, this is proportional to the concentration. It thus follows that the polarographic method is both quantitative and qualitative, the deposition potential indicating the nature, and the diffusion current the amount of the material undergoing electrolysis.

As the application of polarography is dealt with in Chapter IX on microchemical methods, no further discussion is given here.

AMPEROMETRIC TITRATIONS¹

These have as their basis measurement of the diffusion current of the substance to be determined. The principle of the method is to

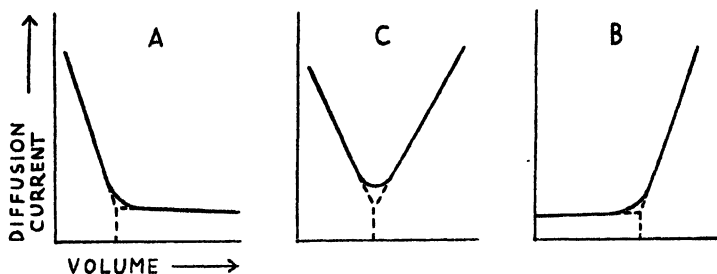


FIG. 59. Typical Diffusion Current-Titrant Volume Curves.

polarize a micro-electrode (which may be a dropping mercury electrode or a small solid metal electrode) to give a diffusion current due to the substance being determined. The solution is kept stirred and a reagent titrated into the solution. The diffusion current decreases as the active material is consumed and at the end point the volume-current curve changes direction.

Typical diffusion current-titrant volume curves are shown in Fig. 59.

¹ See also Chapter IX, p. 397.

Excellent surveys of the method have been given by Stock^{1, 2} with full details of the apparatus required. Although the dropping mercury electrode may be employed for these titrations, rotating or vibrating platinum micro-electrodes have been shown to have advantages in a number of cases^{3, 4}.

Applications of amperometric titrations to mineral analysis are extremely numerous. A few only are listed below, zinc with ferrocyanide⁵, thorium with fluoride⁶, potassium⁷, calcium, and fluorine⁸.

¹ J. T. Stock, *Analyst*, **72**, 1947, p. 291.

² J. T. Stock, *Metallurgia*, **37**, 1948, p. 220.

³ I. M. Kolthoff, D. R. May, P. Morgan, H. A. Laitinen and A. S. O'Brien, *Ind. Eng. Chem. Anal.*, **18**, 1946, p. 442.

⁴ E. D. Harris and A. J. Lindsey, *Analyst*, **76**, 1951, pp. 647, 650.

⁵ J. J. Lingane and A. M. Hartley, *Anal. Chim. Acta*, **11**, 1954, p. 475.

⁶ M. Sundaresan and M. D. Karkhanavola, *Current Science*, **23**, 1954, p. 258.

⁷ W. Kemula and J. Kornacki, *Roszy, Chem.* **28**, 1954, p. 635.

⁸ O. A. Songina, A. P. Voiloshnikova and M. T. Kozlovskii, *Izv. Akad. Nauk Kazakh, S.S.R.*, **6**, 1953, p. 669.

CHAPTER XI

SPECTROGRAPHIC METHODS OF MINERAL ANALYSIS

D. W. Wilson, M.Sc., F.R.I.C.

Principles—Range and Limitations—Excitation Sources—Spectroscopes and Spectrographs—Photography of Spectra—Sampling and Contamination—Qualitative Analysis—Quantitative Analysis—Measurement of Line Density—Precision and Accuracy—Applications to Mineral Analysis—Selected Bibliography.

PRINCIPLES

THE 'colour' of light is dependent on its wavelength, which is measured in Ångström Units, or angstroms (Å). (One Å = 10^{-10} metre). A prism or a diffraction grating will disperse light into its component wavelengths, producing a spectrum which may be observed by the eye using a spectrometer, recorded photographically by a spectrograph or detected by light-sensitive electronic equipment. The range of wavelength used in spectrochemical analysis is generally limited to the photographic range, which includes the ultra-violet (2,200Å–4,000Å), the visible (4,000Å–7,500Å) and the near infra-red (7,500Å–9,000Å). These wavelengths are approximate, as the response of both a photographic plate and the human eye can vary considerably. Below about 2,300Å, however, photographic gelatin, and below about 1,900Å air, absorb some of the light. The region above 9,000Å, although of importance in infra-red absorption analysis, is of little interest in spectrochemical work.

Light may be classified according to the physical condition of its source. Incandescent solids and liquids (*e.g.* molten metals) emit light which contains all wavelengths over a wide range. This, when analysed by a spectrograph, gives a *continuous* spectrum (Pl. 12a) which, since it depends on temperature rather than on nature of the incandescent material, is of no value for identification. In addition, the background which it produces can complicate quantitative work. Incandescent vapours consisting of molecules emit light of specific wavelengths. They give *band* spectra (Pl. 12b)

which are characteristic of the molecules present. Few band spectra, however, are found in spectrochemical analysis, since under usual conditions of excitation most molecules are broken down into atoms. Occasionally the recognition and intensity of a particular band can be diagnostic, but they more often mask otherwise useful regions of the spectrum. When the incandescent vapour consists of atoms and ions, the specific wavelengths give *line* spectra (Pl. 12c and 12d), which form no easily recognised pattern, and may vary from a simple spectrum, of relatively few lines, to a complex spectrum requiring good dispersion to resolve it into single lines. The lines are characteristic of the elements which produce them and line spectra are almost invariably used in spectrochemical analysis. The nature of the phenomena which cause these different kinds of spectrum is beyond the scope of this chapter; the reader is referred to the general texts in the Bibliography (p. 431) for further information.

Not all known elements give spectra under the usual conditions of spectrochemical excitation. To produce the spectra of the inert gases, nitrogen, oxygen, sulphur and the halogens (except fluorine which, as the CaF molecule, produces a useful band spectrum) requires a special discharge; these elements are usually regarded as being outside the scope of ordinary spectrochemical analysis. The remaining elements, *i.e.* the metals, both main group and transition, together with boron, carbon, silicon, phosphorus, arsenic, antimony and selenium, can produce spectra which can be used, albeit to varying degrees of certainty, in their recognition and determination. Their spectra can vary in nature from carbon and selenium, with only a few lines, to the transition metals, whose spectra can be exceedingly complex.

The spectrum of an element depends on intensity of the energy of the source. Below a certain energy, called the resonance potential, which varies considerably from element to element, no spectrum is produced. As the energy is increased, a few spectrum lines appear first. These are also the last to disappear with decreasing concentration of the element, and are called the persistent lines, or *raes ultimes*. They are obviously of considerable importance in spectrochemical analysis. Energies insufficient to ionize the atoms produce *arc* spectra, so called from the usual method of excitation, and often designated by the Roman numeral I. Higher energies produce successively lines due to singly, doubly, etc., ionized atoms, which are called *first spark* (II), *second spark* (III), etc. respectively. The arc spectrum of an element can differ considerably from the spark spectra; although an arc will usually produce some spark lines and *vice versa*, the nature of the excitation must be kept in mind when comparing spectra.

RANGE AND LIMITATIONS

Spectrochemical analysis requires a sample of only a few milligrams of material, which may be an original sample or a chemical concentrate. Recognizable spectra can be obtained with elements which constitute, in very favourable cases, 0.0001% of the material. When more than one spectrochemical element is present, the spectrum of each is produced, and although the intensity of a spectrum can be profoundly altered by accompanying elements, the method lends itself to simultaneous detection of a number of elements in a complex material.

Elements present in small percentage can be determined indirectly by comparing intensity of their spectra with those of known standards. Rapid visual methods can give values which may lie within 50% of the true value. More precise but more tedious methods can reduce this figure to 2–10%, depending on the nature of the sample. Although major constituents are best determined chemically, and elements present in the 20–0.01% range can sometimes be determined colorimetrically with a high degree of accuracy, spectrochemical analysis in lower ranges is seldom surpassed in accuracy by other methods.

Spectrochemical methods are not, however, suited to isolated analyses. The instruments are elaborate, and their best use is achieved only by long experience.

EXCITATION SOURCES

A FLAME SOURCE has the lowest energy of excitation. A bunsen flame may be used, but more elements are detected and more of their lines produced by using oxygen with coal-gas, acetylene or hydrogen. Such a source reaches a temperature of up to 3,000°C and is capable of exciting the spectra of some thirty elements.

A solution of the sample is usually fed into the flame as a fine spray from an atomiser (Lundegårdh method). It has particular application to the determination of the alkali and alkaline earth metals in soil samples¹ where its ease of control, steadiness and low background are an advantage. The necessity for a solution of the sample limits its use in general mineral analysis.

The DIRECT CURRENT ARC is the most widely useful source for both qualitative and quantitative mineral analysis. Direct current voltages of 100–250 volts are usually employed and are applied through a tapped or sliding resistance (which should permit currents of 2 to 12 amps to be carried) to electrodes held in an insulated arc

¹ R. L. Mitchell, Applications of Spectrographic Analysis to Soil Investigations, *Analyst*, 71, 1946, p. 361.

stand. This allows movement of both electrodes together in focusing the arc on the spectrograph, and independent vertical movement of the top electrode to set the arc gap, which is usually 3–5 mm. The arc is struck by lowering the top electrode momentarily to touch the lower one, or by touching both with a clean carbon rod or, better but more complicated, by means of a brief high-voltage pulse which initiates the direct-current arc.

In the unlikely event, in mineral analysis, of the sample being itself a good conductor and of a suitable shape, it may form the electrodes with the advantage that no extraneous material is introduced into the arc. More often the electrodes are rods of specially purified carbon, generally as graphite, and the powdered sample, often mixed with powdered graphite, is placed in a hollow drilled in the lower electrode. Solutions can be soaked into the tip of the lower electrode or evaporated to dryness in the cavity. The upper electrode is usually somewhat pointed to minimize wandering of the arc.

Graphite has the advantage of being readily shaped and has itself a very simple spectrum, although bands due to the CN molecule can be troublesome. The carbon spectrum and the CN bands are often largely suppressed by the presence of the sample, and the bands may, if required, be eliminated by running the arc in a nitrogen-free atmosphere. Ordinary spectrographic graphite contains a few impurities, commonly Ca, V, Ti, Fe, Si and B, which are present in such small quantity that only a few lines of each appear. They are often undetectable by arcing the electrodes alone but the presence of a sample tends to emphasise them. Graphite rods of special purity are obtainable; occasionally metal electrodes, particularly copper which has a relatively simple spectrum, can be used with advantage.

During arcing, the anode (positive pole) is hotter than the cathode, so vaporization of the sample occurs more rapidly when the lower electrode is the anode. With small samples, however, slower vaporization can be an advantage and, in addition, when the cathode (negative pole) is made the lower electrode there is an enriched zone of emitting material adjacent to its tip, due to its attraction for cations. This enriched zone, or *cathode layer*, when focused on the spectrograph, is claimed by many workers to give increased sensitivity. The effect largely disappears, owing to cooling of the arc, when the sample is greater than about 10 mg.

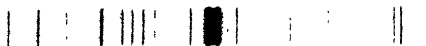
Although it is the most sensitive and versatile source for mineral analysis, the simple d.c. arc has the disadvantages of flickering and wandering, which can result in a lack of reproducibility. A constant-current d.c. arc has been devised to improve the steadiness, and an intermittent a.c. arc, which has many of the characteristics of the



a. Continuous Spectrum.



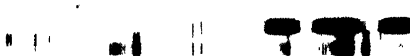
b. Band Spectrum.



c. Line Spectrum (Cu).

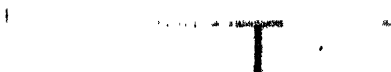


d. Line Spectrum (Fe).



e. Carbon Arc.
Carbon + Al Si sample.
Carbon - Al
taken through Hattmann Diaphra.

A. CONTINUOUS, BAND, LINE AND CARBON ARC SPECTRA.



f. Spectrum of Copper ta
with small, medium and l.
quartz spectrographs



B. COPPER SPECTRUM.

d.c. arc, combines sensitivity with very much improved reproducibility. Versatile but expensive units have been designed which will provide, with a minimum of adjustments, sources of varying characteristics. They can be combined with an automatic timer and have advantages where many and varied analyses are carried out.

The high-voltage ALTERNATING CURRENT SPARK provides the highest energy source for spectroscopy. It excites the spark spectra of the elements and suppresses the arc lines; although it is better than the arc for excitation of such elements as B, C, Si, P and Te, its sensitivity is lower. It has the advantage of superior reproducibility but although widely used in quantitative analysis of alloys it is not readily adaptable to deal with non-conducting powders. It has, however, been used for the analysis of mineral solutions.

SPECTROSCOPES AND SPECTROGRAPHS

The spectrograph produces a succession of images of the light source, corresponding to wavelengths of light emitted by that source. If the source is broad, images will overlap and will be valueless for measurement. The light is therefore passed through a narrow vertical slit (accurately aligned with edge of the prism or with rulings on the grating) and focused (although not strictly true with a grating instrument, which alters the optical geometry of the slit) so that repeated images of it, forming the spectrum lines, are as sharp as possible.

It is clear that the slit is a most important part of the instrument, since any imperfections in it, particularly in a prism instrument, are reproduced on each spectrum line. The slit of a prism spectrograph generally carries two diaphragms, one to alter its length, thus altering width of the spectrum; the other, the Hartmann diaphragm, to permit a number of spectra to be photographed side by side through staggered apertures which are moved successively in front of the slit (Pl. 12e).

Light from the source, having passed through the slit, is dispersed into its component wavelengths either by a prism or by a diffraction grating. Both methods have their protagonists; a brief consideration of merits and disadvantages of each will be given.

A prism produces a single spectrum, so that all light gathered by the spectrograph is concentrated in this spectrum. A grating, however, produces successive spectra (first order, second order, etc.) in which a particular line will appear at multiples of its wavelength. Although intensity of the higher multiples is small and shape of rulings on the grating can be controlled to concentrate most of the light into a particular spectrum, intensity is still generally lower than that of a comparable prism spectrum. Since the successive

spectra overlap, there is the possibility (small in practice) of confusing a longer wavelength line of one spectrum with a shorter wavelength line of the next. The dispersion of the spectrum produced by a prism varies with wavelength, being many times greater at $2,000\text{\AA}$ than at $8,000\text{\AA}$. This has the effect of crowding the lines at the red end of the spectrum, although it can be somewhat minimized by using a glass prism, which has greater dispersion, for the red end and a quartz prism for the ultra-violet, where glass is opaque.

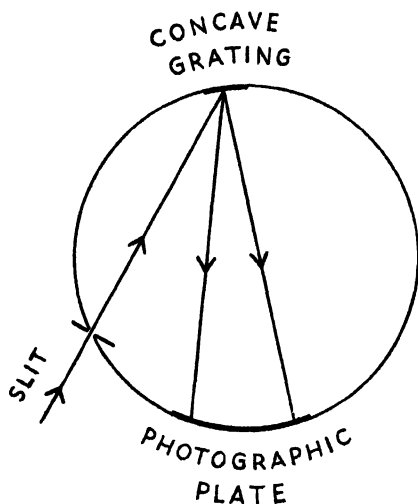


FIG. 60. Concave Grating.

Dispersion of a grating, however, is nearly constant at all wavelengths of a particular order of spectrum and, since it is doubled with a doubling of the spectrum order, the higher orders may, despite their lack of intensity, serve the occasional purpose of separating lines not otherwise clearly resolved. While a prism instrument requires a lens system (which, like the prism, must be of quartz for the ultra-violet region), a grating can be ruled on a concave surface to provide its own focusing (Fig. 60). Because of the focusing characteristics of a grating, however, controlling diaphragms, which on a prism instrument can conveniently be mounted on the slit, must be mounted at an experimentally determined distance in front of the slit, or against the photographic plate. Gratings have other defects; these can be minimized by suitable design of instrument.

In spite of the advantage of constant dispersion which a grating spectrograph possesses, prism instruments are probably more widely employed for analytical work. The most useful analytical region is from 2,500Å to 4,000Å, where dispersion of quartz spectrographs of various sizes and designs is sufficient for most purposes. If utmost versatility is required, there is no doubt that a grating instrument will facilitate examination of the red end of the spectrum.

Visual instruments, or spectroscopes, can give only limited information in mineral analysis. Apart from their restriction to the narrow visible region, the unsteadiness of the source often produces flickering lines which are difficult to observe. Within these limitations, however, there are two useful instruments.

The DIRECT VISION SPECTROSCOPE contains a train of several prisms (Fig. 61), whose refractive indices are arranged to give a spectrum which deviates only to a small extent from the line of incident light and which has an effective length of a few mm. This is a pocket instrument which, with a flame source, may be used in the field, but its only application to minerals is in the recognition of a very few elements whose visible lines in such circumstances are sufficiently characteristic.

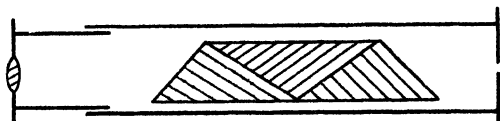


FIG. 61. Direct Vision Spectroscope.

The CONSTANT DEVIATION SPECTROMETER (Fig. 62) enables measurements of wavelengths of spectrum lines to be made with an accuracy of a few angstroms. The prism is constructed so that the light rays are reflected internally from one face and incident and emergent rays are at right-angles to one another. The collimator, providing parallel light for the prism, and the telescope, through which the spectrum is observed, are therefore fixed, the spectrum being scanned by rotating the prism by means of a drum calibrated in wavelengths. Measurement is made by aligning the spectrum line with cross-hairs or a pointer contained in the eyepiece. The telescope of the spectrometer may be replaced by a camera attachment, thus turning it into a spectrograph. Since a photographic plate builds up a record of the light received during the time of exposure, difficulties of observation due to unsteadiness of the source are minimized. For analytical work, however, the instruments used are generally constructed solely for photography.

The SMALL AND MEDIUM QUARTZ SPECTROGRAPHS (Fig. 63) employ a 60° quartz prism (made up of two 30° prisms arranged so that the

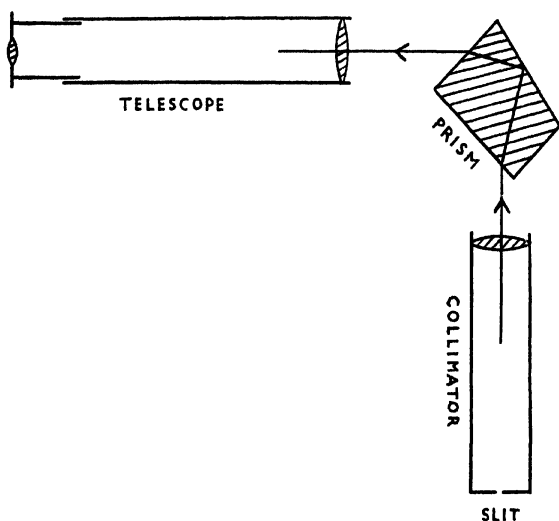


FIG. 62. Constant Deviation Spectrometer.

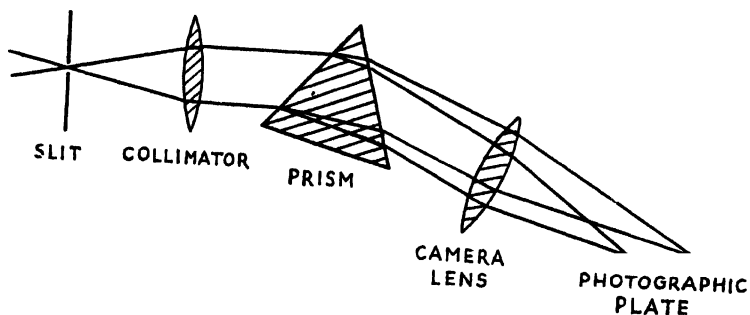


FIG. 63. Small and Medium Quartz Spectrograph.

natural optical rotation of the quartz cancels out) and quartz lenses to record a spectrum of effective length of about 7 cm. and 18 cm. respectively for the 2,200Å to 8,000Å range. Both instruments record this range on a single plate, of importance when the sample permits only one exposure from which maximum information must be obtained.

The low dispersion of the small instrument makes it generally suited only to qualitative analysis for elements such as Mg, Cu, Al, Ag, having relatively simple spectra. The greater dispersion of the medium instrument is adequate for quantitative as well as qualitative work involving a large number of elements. Instruments of this type (Pl. 13A) are probably the most generally used for spectrographic analysis.

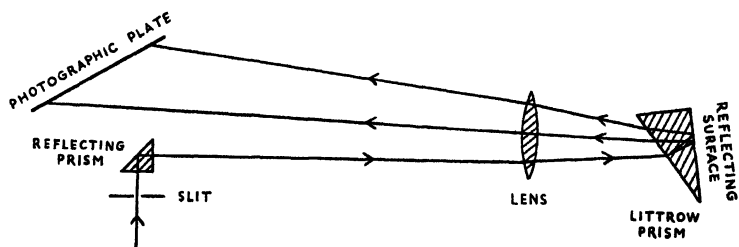


FIG. 64. Littrow Prism.

The LARGE QUARTZ SPECTROGRAPH (Pl. 13B) extends the spectrum range to about 64 cm., this range being usually recorded on three 10 in. plates. The greater dispersion, required for complex spectra of such elements as Ti, V, Cr, Mn, Fe, Co, Ni, Mo, W, U and rare earth elements, is obtained by using a Littrow prism (Fig. 64); this is a 30° prism with a reflecting back, the total dispersion thus being equivalent to that of a 60° prism. The greater effective dispersion is obtained by making use of the full length of the instrument for the dispersed beam. Since light passes through the prism in two directions, no correction for optical rotation is required, and one lens serves both as collimating and camera lens. The region of spectrum to be photographed is selected by a calibrated drum rotating the prism table and automatically correcting focus of the lens and tilt of the camera. Plate 12f compares dispersion of part of the copper spectrum produced by small, medium and large quartz prism spectrographs.

In these instruments the quartz train may be replaced by glass to give greater dispersion at the red end of the spectrum.

PHOTOGRAPHY OF SPECTRA

Wavelength measurement is assisted by rigidity of photographic plates, available in thin glass necessary for slightly curved plate-holders of some instruments. For qualitative work, film has an

advantage in storage space and a film attachment may be used holding a spool of 35 mm. film which can be chopped for processing after each series of exposures.

Medium to fast emulsions are needed for qualitative work. They give high sensitivity with corresponding sacrifice in contrast and resolution. Ideally, quantitative work requires a slower emulsion in which sensitivity may be lower, but contrast between lines of differing density higher. In mineral analysis, however, contrast of the faster plates is generally adequate and is much more constant over the length of the spectrum¹. This can be an advantage when densities of lines of different wavelengths are to be compared.

The effective lower wavelength limit of photographic emulsion, due to absorption by gelatine, is about 2,300Å. The upper limit of non-sensitized emulsions is about 5,200Å, *i.e.* they respond to ultra-violet and blue regions only. Where a higher limit is required, panchromatic emulsions may be used to about 6,500Å and specially long-range plates are available with a limit of about 8,800Å for elements, particularly potassium, whose most useful lines lie in the far red region.

In qualitative work, where the plate is not required subsequently as a record, processing and, in particular, fixing can be cut to a minimum. For quantitative work and where the plate should be retained (it is usually a mistake to discard a successful plate, since reference to it may be valuable in a future problem) processing must be meticulous.

SAMPLING AND CONTAMINATION

In any form of analysis preparation of a representative sample and protection of the material from contamination are of importance. In spectrochemical analysis of minerals, where the analysis sample is often exceedingly small compared with the specimen, and where sensitivity of the method is great, the problems involved are increased. Sampling procedures follow normal practice but rigid precautions must be taken against contamination from crushers, mills, mortars and sieves. Roughening and pitting of a crushing or grinding surface will inevitably give trouble. Sieving which involves rejection of particular fractions may result in a non-representative sample.

Spectrographic procedures must be carried out with a view to excluding possibility of contamination. Electrodes should never, for instance, be inserted tip first into their holders, as these are

¹ E. H. Amstein, The Effect of Wave-length on the Contrast of Photographic Plates in the Ultra-Violet, *Journ. Soc. Chem. Ind.*, 63, 1944, p. 172.

inevitably coated with fine dust from previous analyses. Reference or comparison spectra should be run after that of the sample, to avoid contamination from fine condensed material floating in the air.

QUALITATIVE ANALYSIS

This may be performed as a preliminary to chemical or quantitative spectrographic analysis or it may in itself be the sole information required. In any case it involves identification of the spectrum lines produced by the sample. The spectrum may be viewed directly or with a magnifier on a simple viewing-stand, where the plate is placed on an opal surface which is evenly illuminated from below. It may be projected on to a white screen in a spectrum projector (Pl. 14), where the plate may be moved to bring any desired portion into the field of view. The projected image may also be brought into conjunction with annotated photographs of comparison spectra, obtained from a standard plate by enlargement through the same projector. If the problem is the simple one of searching for presence of a particular element, a reference spectrum of that element is photographed in conjunction with that of the sample, using the Hartmann diaphragm, and lines common to both spectra are looked for.

Where complete qualitative analysis is required, an experienced operator will usually recognize characteristic groupings belonging to some of the elements present; the problem is simplified if a comparison spectrum of a major constituent already known to be present has been photographed in conjunction with that of the sample. The unknown spectrum is compared with spectra of each of the recognized elements in turn and each identified line can be spotted out in ink in the plate. These comparisons with spectra on other plates are facilitated by a comparator. The JUDD LEWIS COMPARATOR is a visual instrument which brings enlarged images of corresponding portions of spectra on two plates in conjunction in an eyepiece (Pl. 15). It carries a fine scale to assist in measuring distances between lines. A PROJECTOR COMPARATOR is a more complex instrument which projects the images in greater enlargement on to a screen.

Lines which remain unknown and which cannot be recognized (the number of these will be inversely proportional to the experience of the operator) must have their wavelengths measured. The wavelength scale, which in some spectrographs is printed on the plate, is not sufficiently accurate to be used for this; it is done by interpolation between known lines, one on either side, either in the same spectrum or in a reference spectrum which has been photographed in conjunction. Common reference spectra are those of copper for

a spectrograph of medium dispersion, iron for one of high dispersion. Maps of these spectra are to be found in many reference books, e.g. W. R. Brode (Bibliography, p. 431) and the wavelengths of the known lines are obtained from these or from wavelength tables. Distances between these lines, and between one of them and the unknown, are measured using a magnifying scale or a travelling microscope of low power. The wavelength of the unknown line is usually calculated by a simple linear interpolation, a process accurate with a grating spectrum; with the variable dispersion of a prism spectrum, it can only be applied if the lines are close together. Reference is then made to a table of spectrum lines of all elements arranged in order of wavelength. The most comprehensive of these are the M.I.T. Tables (Bibliography, p. 432), but abridged tables are to be found in many textbooks. Due attention should be paid to intensities given in the tables for the source used.

It is seldom that an unequivocal identification can be made of a single line, as there are usually several possibilities listed in the tables. A possible element is chosen and its *raes ultimes* (found in tables of spectra arranged by elements) looked for. If they are not present, the next possibility is examined; when the element has been identified in this way, its lines are spotted on the plate as they are identified from the tables. This procedure is continued until no further unknown lines remain.

When the unknown contains traces of many elements with complex spectra, this method can be tedious, although increasing ability of the operator to recognize complete spectra, rather than individual groups of lines, will facilitate diagnosis. The method can, however, be simplified by using for comparative purposes the spectrum of *R.U. Powder*. This is a mixture, in a base of zinc, calcium and magnesium oxides, containing 50 elements in such proportion that only the *raes ultimes* (in practice about 7 lines) of each element are excited. Its spectrum is photographed on a reference plate or, using the Hartmann diaphragm, in conjunction with the spectrum of the unknown. The map of the *R.U.* spectrum, in which each line is identified by wavelength and element, enables identification to be readily made.

Identification of spectrum lines by any method requires a combination of common sense and perseverance. To report the presence of an element on the strength of a few lines when its *raes ultimes* are absent is, without other evidence, as faulty as missing an element through incomplete examination of the plate. Qualitative spectrographic analysis must also have a quantitative aspect when more than one element is present. The analyst must be prepared to report principal constituent, major constituents, minor constituents and traces. This involves visual assessment of intensities of comparable

lines and of the number of lines due to each element. It is complicated by the considerable effect which the presence of one element may have on the intensity of the spectrum of another; this may be assessed by comparisons with reference plates of spectra, taken under the same conditions, of similar materials whose quantitative composition is known. The most valuable asset of a spectrographer, next to his instruments and his experience, is an extensive and well-indexed library of plates of spectra of the materials with which his work is concerned.

QUANTITATIVE ANALYSIS

The intensity of an emitted spectrum line is, under given conditions, effectively proportional to the quantity of element which emits it. The blackening which the line causes on a photographic plate is, for a reasonable intensity range, linearly related to the logarithm of its intensity. Hence, within wide limits, the line density on the plate gives a measure of the quantity of element present in the sample. In practice this density is compared, either visually or photometrically, with densities of a series of standard samples containing known percentages of the element and produced under the same conditions.

Since, as mentioned above, the spectrum of an element can be considerably modified in intensity by other elements present, these calibration standards should ideally be of identical composition, except for the element sought, with the analysis sample. The best standards are accurately analysed samples of the mineral itself, which contain varying percentages, over the desired range, of the element. It is seldom that this can be achieved, but it may be possible to obtain a specimen of the mineral free from the particular element. This is used as a base material and a weighed portion of it is thoroughly incorporated with a suitable weight of a pure compound of the element. Portions of this mixture are quantitatively diluted with more base material to give a range of standards containing known concentrations of the element.

If such a mineral sample is not available, the base material must be synthesized. Many such synthetic bases have been recommended¹ and some are suitable for a range of mineral compositions. They are often mixtures of high purity Na_2CO_3 , SiO_2 , and Al_2O_3 with CaO , MgO , Fe_2O_3 , TiO_2 , K_2SO_4 etc., to correspond as closely as possible to the mineral type being analysed. They are usually sintered after mixing to improve the burning quality of the arc, and for the same reason are often mixed with powdered graphite before arcing.

¹ L. H. Ahrens, Bibliography, p. 432.

It is possible to incorporate several analysis elements in appropriate concentrations in one base material.

The densities of the lines due to the element in the sample and in the standards can be matched visually. More accurately, the densities of an appropriate line in the standards are measured instrumentally, the plate background being taken as zero (see below) and graphed, usually on log paper, against the percentage of the element present. This gives a working curve to which the density of the same line in the sample is referred. Although the arcing samples must be weighed, this procedure is rapid once the standards have been established, and it is used widely in mineral analysis.

There are, however, variables in the excitation of the arc and in the processing of the plates which make direct measurement of line density unsuitable (although there are exceptions) for work of the highest accuracy. To compensate for these variables, the method of INTERNAL STANDARDS is used. Each measurement of line density is made, not directly against the plate background, but as a ratio to the density of a line due to another element (the internal standard), which is present in constant percentage in both the sample and the calibration mixtures. Ideally, any variations in source and in procedure will effect the analysis line and the internal standard line equally, and so will cancel; hence, since a ratio is being measured, the arcing samples need not be weighed.

For the method to be effective, lines which are to be compared, *line pairs*, must be carefully chosen. Both must be due either to atoms or ions, otherwise variations in arc conditions will affect them unequally. They should be close together to minimize differences in response of the photographic emulsion to different wavelengths; they must be of comparable intensity to reduce errors in the ratio measurements. The internal standard must volatilize in the arc at a similar rate to the analysis element. Where *line pairs* have the same excitation properties, so that they are equal in intensity for given concentrations, under fluctuating arc conditions, they are known as *homologous pairs*.

In the analysis of alloys, it is usual to take the major constituent, which is deemed to be present in both sample and standards in effectively constant percentages, as the internal standard, and lines of suitable position and intensity are chosen as reference lines for the minor constituents. This convenient practice is seldom possible in mineral analysis, since there is not usually a suitable element present in sufficiently constant proportions. The internal standard must therefore be incorporated, in constant concentration, in the sample and calibration mixtures. The compound, usually the oxide, containing the internal standard must, of course, be checked carefully for absence of the element which is being determined.

Conversely, constancy of percentage of the chosen standard will be adversely affected if it is already present in appreciable quantity in the mineral or base material. The actual percentage of standard added is immaterial provided a line of suitable intensity can be chosen. In some cases, of course, it is inadvisable to dilute the sample more than is necessary.

Many internal standards have been recommended for specific analyses. Others have been described as suitable for groups of minor constituents which have similar volatility in the arc. The choice in a particular case must always be experimentally confirmed.

MEASUREMENT OF LINE DENSITY

There are two general methods for measuring line density and density ratios. The first employs a ROTATING SECTOR, which is a metal disc with its periphery cut either in a series of logarithmic steps (step sector) or along a logarithmic curve (log sector). The cut-away portion revolves, at speed, immediately in front of the slit, or with a grating spectrograph at a focus point some distance from the slit, so that the quantity of light falling on the slit is decreased logarithmically in intensity towards the centre of the sector. The resulting spectrum lines are tapered in appearance, either stepwise or smoothly. The base corresponds to the extreme edge of the disc which passes the most light and the length of the line is a direct measure of intensity of the light emitted at that wavelength. This length is measured with a suitable scaled magnifier in tenths of a millimetre.

The second, nowadays the more usual, method measures the density of the photographed line (which is not cut down in intensity) by means of a MICROPHOTOMETER or densitometer. The plate is slowly traversed across a slit through which passes a beam of light, which then passes through another slit to a photocell. The current produced is controlled by a rheostat and directed either to a mirror galvanometer (non-recording microphotometer) or, by suitable amplification, to a pen recorder (recording microphotometer). Using the non-recording instrument, the rheostat is adjusted to give full-scale deflection with the plate background. The spectrum line is then passed slowly through the light beam and the minimum deflection, corresponding to the maximum intensity of the line, is read. The recording microphotometer, in which rate of travel of the plate is controlled by a variable-drive motor, gives a pen trace of the intensity of the line. Both instruments generally use a linear scale of density; thus the working curve is prepared by plotting log density, or log density ratio if an internal standard is employed, against percentage composition or log percentage composition.

PRECISION AND ACCURACY

Successive spectrographic determinations of a particular element in a specimen will, as in other methods of analysis, show a spread of results. The narrower this spread, the greater is the reproducibility or precision of the method. Since spectrographic determinations are carried out by reference to standards, lack of precision is due to inadequate elimination of, or compensation for, variables of sampling, light source, processing and measurement. If these are truly random, as is usually the case where the spread is fairly uniform and not excessive, a mathematical measure of the precision can be obtained. Clearly an expression such as ' $\pm 20\%$ ' is of limited value, since it gives no satisfactory information on the nature of the spread normally encountered.

All useful measures of precision are commonly based on the standard deviation of the results obtained in a series of determinations run under the precise conditions recommended for the analysis. The definition and properties of standard deviation are outside the scope of this chapter, but will be found in any textbook on elementary statistics¹.

Unfortunately, there is no general agreement on the function of standard deviation which is used in reporting spectrographic results; even the names given to such functions can be misleading. It is often expressed as a percentage of the mean value for the analysis. For example, if the standard deviation is 0.002 on a mean value of 0.025% of element present, it would be expressed as 8%. The accuracy of this measure increases with the number of determinations on which it is based, and with such a rapid method as spectrography this number should always exceed 10, and preferably 20.

Generally accepted statistical limits for analytical work are such that 19 out of 20 results are included within them. These limits are approximately given by $2 \times$ standard deviation. For example, if the standard deviation of a method, expressed as a percentage of the mean value, is 8%, then 95% of future determinations, using the identical procedure, will probably fall within $\pm 16\%$ of the mean. Replicate analyses serve to reduce these statistical limits. An average of four determinations, for instance, will probably lie within approximately plus or minus the standard deviation. Some such mathematical expression of precision is imperative when two methods are compared; it should be regarded as an essential in reporting the performance of a method.

A method which has a high precision may, however, be inaccurate, *i.e.* it may give repeatable results which differ systematically from

¹ See Chapter XVI.

the true one. Accuracy is often difficult to establish in spectrochemical work, since it involves analysis of samples whose quantitative composition is accurately known by other, e.g. chemical, means. In many cases where trace elements are concerned, no other means may be found to give a figure comparable in accuracy with the spectrographic one. Lack of accuracy in a method of good precision is usually due to some systematic difference between procedures used for the calibration curve and for the sample. A frequent cause is difference in basic composition of the standards and the sample, giving unequal modification of intensities of the lines of the internal standard and the element sought.

APPLICATIONS TO MINERAL ANALYSIS

Qualitative and quantitative spectrochemistry have always had a close connexion with mineralogy. Their techniques were invented for detection of elements in minerals, and their development has owed much to geochemists¹ who recognized that speed and versatility of the methods were well adapted to the complexities of mineral analysis. Many modern geochemical problems, such as the K/Rb ratio, and the minimum age of the earth, have been elucidated by spectrochemical methods².

At the end of this chapter will be found a selected Bibliography. General textbooks may be supplemented by a considerable spectrochemical literature which, fortunately, is well documented^{3, 4}; it may be kept up to date by the annual reviews of analytical chemistry published since 1949 in *Analytical Chemistry*.

There are, in the Bibliography, three references which deal particularly with spectrochemical analysis of minerals and related materials. L. H. Ahrens in *Spectrochemical Analysis* gives an account of techniques of qualitative and quantitative analysis of such materials by the d.c. arc, and describes procedures for individual elements, with useful geochemical comments. The same author's *Quantitative Spectrochemical Analysis of Silicates* co-ordinates a number of procedures for the d.c. arc analysis of natural silicates. R. L. Mitchell, in *The Spectrographic Analysis of Soils, Plants and Related Materials*, deals with flame techniques for soil and mineral solutions. These works list extensive and useful references.

¹ V. M. Goldschmidt, *Geochemistry*, Oxford, 1954.

² L. H. Ahrens, *Appl. Spectroscopy*, 6, No. 5, 1952, p. 11.

³ W. F. Meggers and B. F. Scribner, *Index to the Literature of Spectrochemical Analysis*; Part I (1920-39); Part II (1940-45) and Part III (1946-50). American Soc. for Testing Materials.

⁴ Spectrochemical Abstracts, F. Twyman, I, (1933-37); E. H. S. van Someren, II, (1938-39), and III (1940-45); E. H. S. van Someren and F. Lachman, IV, 1946-51; (Hilger and Watts, London).

A comparison of spectrographic and chemical methods for the determination of major constituents of a granite and diabase has been made in a large scale co-operative investigation¹. Although silicon and aluminium were better determined chemically, a number of other constituents showed greater accuracy with spectrography. Major quantities of silica in minerals have been determined by difference, using a rapid spectrographic method².

A rapid semi-quantitative method has been developed for the analysis of 68 elements with a single exposure in a wide range of minerals, rocks and ores³. A 10 mg. sample is used and the elements are reported as 0.0001–0.001 %, 0.001–0.01 %, etc. Standards for each element are prepared by evaporating solutions on to the electrode to represent percentages decreasing from 10 to 0.0001. The unknown samples are mixed with graphite powder before arcing. A table is given of the comparison lines used for each element. A chemical check on 500 analyses showed 92 % in agreement, with the remainder differing by one bracket. The method may be the sole analysis required, or it may be a preliminary to more accurate spectrographic or chemical analyses. It enabled the authors to complete 245,000 determinations in three years.

The important problem of the mutual interference of elements in the intensities of their spectra has been studied. It has been shown that a spectrochemical series can be evolved, in which an element depresses the spectra of those below it, and enhances the spectra of those above it⁴. Sn, K, Co, Ca and P, in that order, show this effect⁵. Among 'buffering' materials which reduce the effect are lithium tartrate and fine germanium metal, which has been used for geological materials⁶.

Heavy dilution with CuO (which acts as an internal standard) and graphite, and in addition variable dilution with germanium dioxide to give, as far as possible, a constant percentage of element sought to diluted sample, is recommended as a procedure applicable to any powdered sample, whether metallic or non-metallic⁷. The sample and standards have an effective base of CuO–GeO₂–C, and once a working curve has been prepared for an element, all future samples which contain it can be referred to the curve.

Preliminary chemical concentration can give enhanced sensitivity.

¹ W. H. Dennen, L. H. Ahrens and H. W. Fairbairn, *U.S. Geol. Survey, Bull.* 980, pp. 25 and 53, 1951.

² G. Hartleif and H. Kornfeld, *Arch. Eisenhüttenw.* 23, 1952, p. 103.

³ C. L. Waring and C. S. Ansell, *Anal. Chem.*, 25, 1953, p. 1174.

⁴ W. R. Brode and D. L. Timma, *Journ. Optical Soc. Am.*, 39, 1949, p. 478.

⁵ W. G. Schrenk and H. E. Clements, *Anal. Chem.*, 23, 1951, p. 1467.

⁶ L. W. Strock, *Appl. Spectroscopy*, 7, No. 2, 1953, p. 64.

⁷ E. K. Jaycox, *Anal. Chem.*, 27, 1955, p. 347.

A method has been described¹ in which the sample is dissolved in HCl containing indium, which acts as an internal standard and as a collecting agent for small precipitates. Precipitation is carried out by adding successively, with appropriate conditions, oxine, tannic acid and thionalide. The quantities determined ranged from 0.15 to 370 p.p.m.

Improvements in accuracy of flame techniques for Na, K and Ca have been reported. Internal standards have been used for concentrations in mineral solutions of 15–30 p.p.m. and the interference of other ions has been studied².

Refinements in technique and an improved method of evaluating results by dilution, using Co as an internal standard so as to give an optimum intensity ratio of one, have given a standard deviation for Na and K estimations in soils and plant extracts³ of 1.5%. Some of the types of interference encountered have been reviewed⁴.

Sulphur and chlorine, not usually regarded as spectrographic elements, have been detected and determined in solid ash, deposits, etc., by a high voltage discharge technique⁵. Bromine, added as KBr, was used as an internal standard and the sample and standards were prepared in a base of silver powder.

There are no signs that development of qualitative and quantitative spectrochemical analysis of minerals will soon cease. Improvements in sensitivity and in precision are bound to follow advances in the knowledge of the effect which one element has on the spectrum of another. In time the direct photometric measurement of intensity of spectrum lines, without a necessity for the intermediate of the photographic plate, may be capable of application to minerals as it is now, within limitations, to alloys. All that will then be required is a direct evaluation of intensity in terms of quantity, so that calibration standards will no longer be needed.

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(Continued on page 432)

¹ G. E. Heggen and L. W. Strock, *Anal. Chem.*, **25**, 1953, p. 859.

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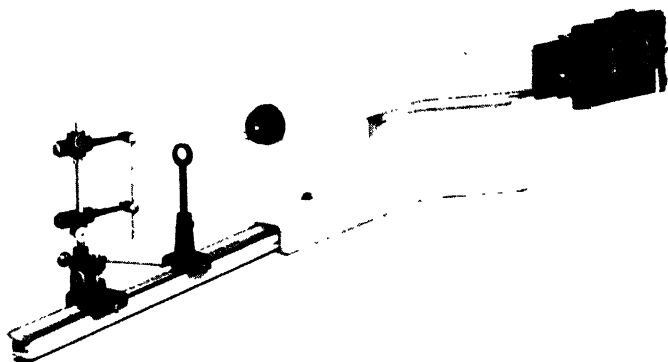
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Wavelength Tables

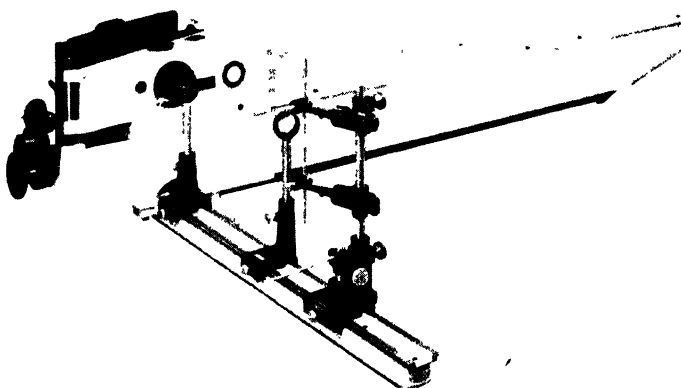
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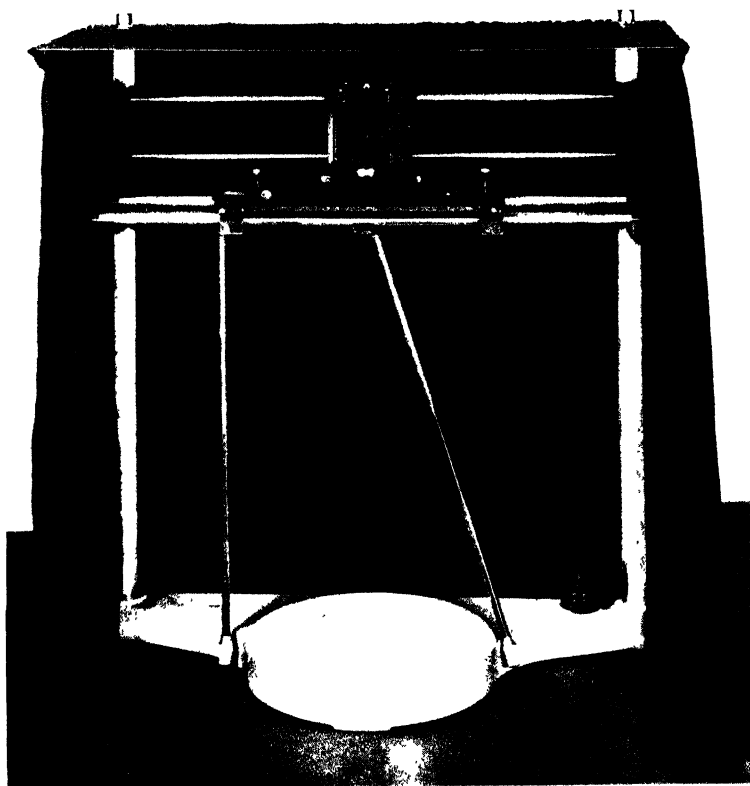
A. MEDIUM QUARTZ SPECTROGRAPH.

(Courtesy Hilger & Watts Ltd., London, N.W.1.)



B. LARGE QUARTZ SPECTROGRAPH.

(Courtesy Hilger & Watts Ltd., London, N.W.1.)



SPECTRUM PROJECTOR.
(Courtesy Hilger & Watts Ltd., London, N.W.1.)



JUDD-LEWIS SPECTRUM COMPARATOR.
(Courtesy Hilger & Watts Ltd., London, N.W.1.)

CHAPTER XII

APPLICATION OF FLUORESCENCE ANALYSIS IN SEDIMENTARY PETROGRAPHY

Julius Grant, M.Sc., Ph.D., F.R.I.C.

Principles—Nature of Fluorescence—Methods: Range and Limitations—Qualitative—Quantitative—Apparatus—Filters—Methods and Technique: General Analysis—Preliminary Qualitative Examination—Capillary Analysis (Paper Partition Chromatography)—Chromatographic Analysis—Spectrophotometers—Photographic Methods—Fluorescence Microscopy—Titration Experiments—Applications of Fluorescence Analysis: Slags—Mineral Fuels—Bitumens, etc.—Minerals—Calcium Minerals—Felspars—Fluorites—Uranium Minerals—Willemite—Gems—Pearls—Mother-of-Pearl—Loadings and Pigments—Bibliography.

PRINCIPLES

A GREAT deal has been written in recent years on uses of ultra-violet light for the purpose of testing as distinct from irradiation, and an impression may have spread that such methods provide a simple, rapid and almost universally applicable means of examination. Unfortunately many claims for them are extravagant and do not bear repetition. If however they are applied with care and under strictly standardized conditions, the methods can yield most useful results and provide a rapid means which may supplement, less frequently replace, the usual methods of sedimentary petrography.

NATURE OF FLUORESCENCE

Fluorescence may be defined as a form of 'luminescence' or emission of light, but it must be differentiated from 'phosphorescence', since it occurs only while the substance concerned is being 'excited' by a source of light, whereas 'phosphorescence' continues after this

source is removed. The simplest theory of its action suggests that rays of the exciting source of light provide sufficient energy for electrons in the atoms of the substance to move from a position near the nucleus of the atom to a more distant orbit. An unstable condition is thus produced and when the electrons return to their original positions, the absorbed energy is liberated again in the form of fluorescent light.

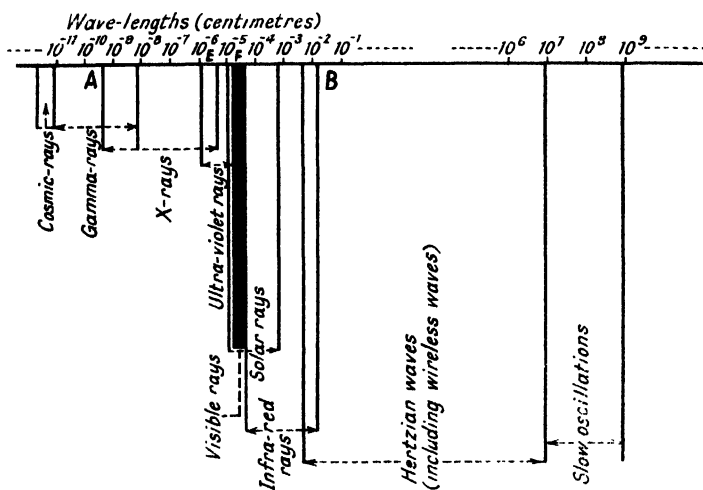


FIG. 65. Ultra-Violet Rays, etc.

It is thus apparent that fluorescence in the strict sense of its definition may occur without being actually visible. Thus, the rays of light emitted may not fall within the range of wavelengths to which the human eye is sensitive, or the exciting light may be so intense as to overpower the fluorescent light it produces. The nature of fluorescence depends on a number of ill-defined factors, such as wavelength of the incident light and, in the case of solutions, on concentration of the fluorescing substance and nature of solvent. Impurities may also stimulate or inhibit fluorescence, *e.g.* pure zinc sulphide is not fluorescent, but a trace of radium, copper, lead, silver, etc., provides the necessary stimulus, though its action is not fully understood.

In cases where a substance emits a fluorescence strictly characteristic of itself, a means of analysis or examination is provided. On the other hand, as already pointed out, this may be masked by brightness of the source of exciting light. There is, therefore, a

distinct advantage in using as such a source rays of light invisible to the human eye. This is the special virtue of ultra-violet light, from which any visible rays may be cut out by filtration, so as to leave only the invisible, though active portion. This is pictured in Fig. 65 where AB represents the known spectrum from x-rays to the infra-red (heat) region. The darkened portion corresponds with visible rays from the sun (rainbow, or solar spectrum) and EF with radiation from a mercury-vapour lamp. The figures represent wavelengths ($1\text{\AA} = 10^{-8}\text{ cm.}$), so that the small portion of the spectrum with which we are concerned may be said to fall approximately between $4,000\text{\AA}$ and $1,800\text{\AA}$. It is now apparent why applications of ultra-violet light methods are so restricted. They are, in fact, normally confined to substances which emit a visible and characteristic radiation under the action of light of the above range.

METHODS: RANGE AND LIMITATIONS

Where luminescence produced is characteristic of the substance irradiated it may be used as a means of analysis. For ordinary work it is sufficient in most cases to note the intensity and colour, but the method is more specific and is applicable to a greater range of materials if the spectrum of the light emitted is examined spectroscopically. In general, intensity of luminescence is proportional to the amount of active substance present and quantitative methods based on these lines have been described. Luminescence, however, is obtainable only from a restricted number of substances; the method is further limited by the fact that it is usually produced only by light whose wavelength falls within a particular range of the ultra-violet region. The usual exciting sources are, however, sufficiently rich in rays of all such wavelengths.

The methods used may be classified as follows:

(1) QUALITATIVE

- (a) *Direct Irradiation.* The substance is placed in ultra-violet light and nature, colour and intensity of luminescence noted and compared with characteristics of that from a genuine sample of known origin. This may be carried out in acid, alkaline or neutral solution, at various concentrations and in a variety of solvents.
- (b) A refinement is to observe luminescence under a luminescence-microscope or to determine its spectral characteristics.
- (c) *Chemical Reactions.* The substance is treated with a chemical reagent which should produce a luminescent compound, and the appearance of such a compound observed. Conversely, if the substance is itself luminescent, a reagent may be chosen which destroys or changes its luminescence.

- (d) *Capillary Analysis* is based on the nature of luminescent zones produced on a strip of filter-paper after it has been soaked in a solution of the sample and dried. Ultra-violet chromatographic analysis and paper chromatography are more recent developments of this technique. The normal procedure in these methods is followed, but the usual methods of inspecting results on the column or paper are supplemented by inspection in ultra-violet light, before or after treatment with suitable chemical reagents which produce or destroy luminescence of the substances present.

(2) QUANTITATIVE

- (a) *Trial and Error*. A number of mixtures containing known quantities of the luminescent substance is compared with the sample in ultra-violet light and an approximate match is obtained with one of them.
- (b) *Photometry*. Intensity of luminescence (other conditions being equal and over a restricted range of concentrations) is proportional to the amount of luminescent substance present and may be determined photometrically.
- (c) *Capillary Analysis (supra)* lends itself to semi-quantitative work if intensity of luminescence of successive zones is measured photometrically.
- (d) *Fluorescent Indicators*. Determinations of pH value may be made by means of indicators whose luminescence in ultra-violet light changes with change in hydrogen-ion concentration. These, and similar compounds, may be used to indicate end-points of, for instance, neutralization or oxidation-reduction titrations. They are usually sensitive in very small quantities and in very great dilutions of reagent and are free from certain of the usual errors inherent in the use of indicators. A change in luminescence of a particular substance on titration with or into a reagent may also be used to determine the substance itself. Further information regarding range and limitations of procedures used will be found under Methods and Technique (p. 440) and in the various examples given in the last section of this Chapter.

APPARATUS

The principal and indeed only really specialized apparatus required is a means of producing ultra-violet light free from visible light. An efficient method of doing so is essential and this matter will therefore be dealt with in some detail.

- (a) *Ultra-Violet Lamps*. The principal sources of ultra-violet rays are the arc-discharges produced by means of mercury, carbon, tungsten or other electrodes, usually in a vacuum. Atmospheric types of lamp do, however, exist, but are not advised for practical purposes; though cheap in initial cost, longer in life, and easily transported, they are

unstable in output, expensive to run and often give off fumes owing to oxidation of the electrodes. Such criticisms apply specially to the carbon arc electrodes (in air) originally designed for therapeutic purposes. It should be remembered, however, that requirements for therapeutic irradiation and chemical examination are quite different. Tungsten electrodes give an extremely stable, permanent and intense light and running costs are not high, although direct current is required. Here again, fumes may prove a nuisance; thus it is not surprising that mercury lamps hold the field almost completely for this type of work.

Several considerations influence choice of a source of ultra-violet light. The ideal source should give conveniently a fairly intense emission of ultra-violet light of all wave-lengths; this intensity should not vary greatly with time or with changes in working conditions. Furthermore, it should be steady in its output, free from objectionable fumes or heating effects and it should be capable of being enclosed and so protected. In fluorescence work, the type of lamp or filter used may influence the results obtained. The combination used in any particular case should, therefore, always be described in published results, so as to allow correlation with results of other workers.

In the luminous discharge lamp the current passes through a vapour or gas contained in a tube or bulb, thus causing emission of light, the spectral characteristics of which are largely governed by nature of the gas in the tube. The spectral radiation from a discharge tube consists of a series of sharply-defined spectral lines, whereas that emitted by the carbon arc-filament lamps or the sun is continuous and consists of radiations from matter at a high temperature. The former tubes emit energy only at certain wavelengths (chiefly in the visible and ultra-violet regions). Thus for fluorescence analysis, a discharge tube provides one of the most efficient sources of ultra-violet light, in addition to its other advantages, although, due to dissipation of energy as heat, efficiency even of the best discharge lamps is only 10–25% of that theoretically possible.

When a potential difference is applied between the two electrodes sealed into the tube, positive ions move in one direction and electrons in the opposite direction, thus producing an extremely small current. While moving, these positive ions and electrons (when travelling above a certain minimum velocity), can transfer sufficient energy to the neutral atom by collision, to displace an electron in the neutral atom and force it into an outer orbit. The new ions produced by collision join the processions to the electrodes and, on their way, come into collision with other neutral atoms. Thus, the process gathers momentum and the current flowing in the tube increases rapidly. This, in turn, causes a fall in effective resistance of the discharge lamp as the current rises. As the current passing is limited by the external circuit (which is necessary to prevent the tube from building up a current large enough to destroy it), the voltage is, in general, inversely proportional to the value of the current allowed to pass. Hence the potential difference required to start the discharge in a tube is greater than that required to maintain it.

In using high-pressure mercury discharge lamps of the type described below for fluorescence analysis, the phenomenon of being unable to re-light a tube soon after switching it off may be experienced. Only when the tube has cooled is it possible to switch it on again. This is because the pressure of the gas in a cold discharge tube is very low, but on running the burner for some time the tube heats up, vaporizing the small amount of mercury present, and the internal gas pressure rises. In this condition the atoms prevent the ions present from acquiring sufficient speed to ionize neighbouring neutral atoms before the collisions between the two types take place.

The usual quartz mercury-vapour lamp can be worked with either alternating or direct-current, at pressures above or below atmospheric; it has spectral range from 1,800Å to 14,000Å. Radiation of wavelengths less than 14,000Å is concentrated mainly in a pair of yellow-green lines at 5,764Å and 5,791Å and a green line at 5,461Å. Radiation of wavelengths less than 4,500Å represents two-thirds of all wavelengths less than 14,000Å. The principal ultra-violet lines are concentrated in a few lines of high intensity, viz. two at 3,650Å to 3,654Å, one at 3,984Å, and possibly another pair between 4,046Å and 4,078Å.

The total radiation of the quartz mercury-vapour lamp increases rapidly with increase in pressure in the tube and depends largely on temperature of the lamp. Since radiation is absorbed by luminous mercury vapour in the lamp, dimensions of the lamp will, to some extent, affect its total output of energy. Physical changes in the quartz in use result in it becoming opaque, and the quartz is also attacked and coated with a layer of the reaction-products of the electrodes. This decrease in intensity affects the short and long ultra-violet and visible portions of the spectrum in nearly equal measure.

After a few thousand hours of operation, the light-emission of a quartz-mercury-vapour lamp decreases to 70 to 80% of its initial value, but by adjusting the power input initially so as to obtain a light-emission of 70% of maximum emission, and gradually increasing it as the lamp ages, a constant intensity can be maintained. Many lamps have an average life of about 2,500 to 3,000 hours and may, even then, usually be cleaned with acid and re-exhausted, a process which may be carried out about three times before the burner is finally discarded. To minimize any clouding effect, temperature of the lamp should be as low as possible: some lamps have a number of thin vanes near the electrodes which circulate a small current of cooling air.

(b) *Commercial Lamps.* A frequently used type is shown in Pl. 16A. It will be seen that the burner is enclosed and that light from the burner passes out through a filter of nickel oxide glass.

In the 'S' lamp of this type now developed by Hanovia, Ltd., the electrodes consist of metal cups coated with electron-emitting salts of the rare earths. It can be made in any desired shape and for operating in any position on either d.c. or a.c. Argon is used to start the discharge and a simple switch is all that is required. Since the mercury content is small, this all becomes super-heated mercury vapour and the burner is not subject to variations of internal pressure within

the normal operating range. Thus, over such normal range, the burner voltage varies by only about 2% for a 10% change in current. The presence of only a small quantity of mercury also eliminates the 'hammer' effect when the lamp is being tilted, with the consequent risk of breakage.

In Model XI (Pl. 16B), the arc-tube is centrally mounted in polished, anodized aluminium reflector, adjustable to any angle between downward and horizontal. A detachable, light-tight cover plate carries a Wood's glass filter (p. 440). The a.c. model consumes 120 watts (d.c. 350 watts) and both a.c. and d.c. models can be adjusted for any mains pressure between 200 to 250 volts. A.C. models (with an auxiliary transformer) can be supplied for operation on supplies down to 100 volts. The useful life of the arc-tube is about 1,000 hours of actual operation.

Hanovia Model XII high pressure mercury vapour arc-lamp (S.220 type) without front filter, gives a powerful mercury-arc beam comprising the characteristic ultra-violet spectrum down to 1,849-5Å. The radiation is a line spectrum, enabling monochromatic bands to be isolated for special investigations. When fitted with the Wood's filter, which is optically polished on both sides, the lamp becomes a high-power lamp for fluorescence analysis.

(c) *Bulb-lamps.* A high temperature discharge of the bulb-lamp type consists of a lamp-bulb made of quartz or glass transparent to ultra-violet light, fitting into an ordinary electric-light holder. It contains tungsten electrodes and a tungsten filament, the heat from which vaporizes a drop of mercury, the arc then being struck between the electrodes. Greater part of infra-red radiation from the lamp comes from the filament, while ultra-violet radiation is emitted from the arc-stream between electrodes.

This bulb is designed for a.c. current only and is used in conjunction with a special transformer. The discharge tube is surrounded by an envelope made of the Wood's glass used for making ultra-violet filters; they are usually fitted with 3-pin bayonet caps or screw-in caps requiring special lamp holders. These lamps generally operate at 195-250 volts, provided the correct choke tapping is used. Average life is about 1,500 hours burning time; emitted radiation is between about 4,100Å and 3,126Å. It is claimed that about 95.5% of ultra-violet radiation is emitted at 3,650Å. These lamps are normally operated by alternating current only and should be used in a horizontal position, otherwise the inner envelope throws a shadow on the object under examination; they cannot, of course, be used where unfiltered ultra-violet light is required.

FILTERS

Filters required for fluorescence analysis are of two main types, viz. to pass ultra-violet light while absorbing visible light and to pass visible light while absorbing invisible light. The former have already been mentioned in connexion with production of ultra-violet light from the mercury lamp. The latter are of importance

when it is desired to photograph a fluorescing object, because such fluorescence usually contains ultra-violet light reflected from the exciting source.

Many types of filters for use in the first category have been suggested, including solid substances, plastics and solutions. Of these however, the so-called Wood's glass is most widely (indeed almost exclusively) used. Wood's glass appears nearly black in ordinary light, as it cuts out practically the whole of the visible spectrum, although it is transparent to most of the ultra-violet region. It is essentially a nickel oxide glass and the best glass appears to have the composition: silica 50%, barium oxide 25%, potassium oxide 15%, nickel oxide 9%, and copper oxide (to cut out red rays) 1%. The spectral and transmission characteristics of such glasses may vary somewhat from batch to batch, even from sheet to sheet.

Many substances, usually solutions, have been proposed for absorbing ultra-violet light while allowing passage of visible light. A 1% solution of cerium ammonium nitrate has, however, been found to be the most suitable¹. This may of course be used in a containing cell having glass walls, because transmission of visible light is desired. Another filter of this type due to J. A. Radley is a 3 mm. layer of a solution containing *o*- or *m*-nitrobenzaldehyde².

By choosing solutions of suitable chemical compositions, or by using cells containing different chemical solutions in series, it is possible to isolate very narrow bands of light of selected wavelengths in the visible or ultra-violet region, by absorbing the unwanted ranges. The filters already dealt with cover most of the ordinary requirements of fluorescence analysis; reference to the literature must be made for others³.

The principal general apparatus required for this work has been described above. In addition there are various minor accessories and specialized apparatus for specific purposes. These are described, as they arise, in the following sections.

METHODS AND TECHNIQUE: GENERAL ANALYSIS

The importance of standardizing and specifying the technique cannot be overemphasized. Differences of apparently minor character have in the past often accounted for contradictory results obtained by different workers using similar materials.

The substance to be examined may usually be placed in a non-fluorescent glass or porcelain dish, and direct observation made

¹ J. A. Radley and J. Grant, *Fluorescence Analysis in Ultra-Violet Light*, 4th ed., (Chapman and Hall, London), 1954.

² *Ibid.*

³ See Bibliography, p. 462.

under the lamp. Containers made from some heavy dark papers, such as black filter-papers, are very effective for solids which give a white fluorescence, but it is preferable to use quartz where possible. Petri dishes may be covered with cellophane. In some cases variations in colour of fluorescence result if the distance from the sample to the lamp is varied.

The substance itself may be in massive or powdered state, or in solution; differences in fluorescence colour may accordingly be revealed. Thus, some substances do not fluoresce when solid but do so when in solution, and *vice versa*. In general, fluorescence appears much brighter if the substance is in the powdered state, although in cases of extreme subdivision it may fade again. Sometimes grinding a crystalline substance finely produces a change in the fluorescent colour.

Solvents may be of great importance; it is often difficult to obtain them free from fluorescence. The fluorescence of many solvents is due to the presence of impurities, and a stringent purification process will therefore eliminate it. Thus, glycerol used as a mounting medium in fluorescence microscopy must be treated with animal charcoal, since ordinary distillation is without effect. These considerations must be taken into account when fluorescence is being used as a measure of the concentration of certain solids in suspension *e.g.*, zinc oxide. Concentration of the solution is another important factor, although this usually affects the intensity of the colour of the fluorescence. In general a rise in temperature reduces fluorescence.

Change in colour or intensity of fluorescence which frequently occurs while a substance is being irradiated may lead to false results if no allowance is made for it. It is of special importance in connexion with capillary analysis and with fading tests. Oxidation, both purely photochemical and as a result of dissolved oxygen or of ozone produced by the lamp, has been suggested as a possible explanation in some cases.

The purity of the substance under examination can in certain instances have an important effect on the nature and intensity of its fluorescence. This indeed is the basis of use of the method for detecting impurities. Minerals provide some interesting examples, *e.g.* artificial willemite fluoresces only if manganese is present, and zinc sulphide requires the presence of copper.

PRELIMINARY QUALITATIVE EXAMINATION

It is emphasized that about 5 minutes should always be allowed for the eyes to acclimatize themselves to the dark surroundings, in order that maximum effect of fluorescence may be appreciated.

This is of particular importance when comparisons of weakly-fluorescing samples are being made. Individuals vary in the length of time required for light-adaptation, and it is good practice for each operator to test himself to determine the minimum time that he, personally, requires.

If the sample is a solid and the surface is fairly large, it may be examined directly in the rays and, at a later stage, photographs taken in daylight and in ultra-violet light compared. The sample should then be broken and the fracture examined under the lamp to see if air and light influence the fluorescence; if so, observations should be made on freshly-broken surfaces. The surface should then be spotted with (a) dilute acid, (b) alkali, and re-examined.

Powders may be examined directly and then shaken up with a non-fluorescent liquid and re-examined. Very fine powders may be blown on to a damp, non-fluorescent filter-paper for examination, but it is best to dry the paper first, as moisture has been shown to change the fluorescence colour of certain fine white powders. Variations in fluorescence intensities or colours with dilute alkali or acid give information as to the acidity or basicity of the powder, whether it is a single compound or a mechanical mixture. The action of heat on the fluorescence of the powder may also be noted.

Liquid samples should be placed in a non-fluorescent (e.g. quartz) tube and examined under the lamp; they should be agitated during the examination. The fluorescence, both at the surface and in the body of the liquid, should be noted, also the fluorescence of the condensate when the sample is boiled. It is often a good plan to dilute the liquid with another, non-fluorescent, liquid and to examine the mixture at progressively increasing dilutions, as a change in intensity or colour of the fluorescence sometimes appears under these conditions; also, there is often an optimum dilution at which fluorescence has a maximum intensity. The tube may be tilted so as to cover the walls with some of the liquid, and this helps to eliminate other colour effects.

CAPILLARY ANALYSIS (PAPER PARTITION CHROMATOGRAPHY)

This is often a very useful method¹ for examination of liquids, especially solutions. If a filter-paper is held vertically with one edge in the solution, it draws up the liquid by capillary attraction; when the wet portion is examined under the lamp, characteristic zones are obtained from many substances. The test does not give comparable results unless a standard procedure is followed.

¹ See also Chapter IX, p. 379.

The paper should be non-fluorescent and should be cut into strips 2 cm. \times 30 cm., all strips being cut in the wire-direction of the sheet, since absorption varies according to the grain of the paper. The paper is then clamped so that it hangs vertically, 5 mm. of the lower edge being immersed in the solution; it may be left for so long as 24 hours in order to ensure that equilibrium is reached. Temperature, concentration, humidity, air currents and time must all be carefully controlled to give comparable results. The papers are then examined under the lamp, and the colour, length and spacing of the various zones produced are compared with those obtained from samples of known compositions and concentrations.

It is obvious that solvents used in this work should be optically inert and non-fluorescent, and ether, petroleum spirit, amyl alcohol and chloroform are widely employed. The choice and purity of the solvent are often important, since different colours may be obtained from the same substance dissolved in a number of different solvents. In aqueous solutions the pH value of the liquid medium is often of great importance.

CHROMATOGRAPHIC ANALYSIS

A number of important classes of substances, including simple and complex inorganic anions and cations, hydrocarbons and dyestuffs, may be separated by the usual technique of chromatography and ultra-violet light has been used for examining the chromatograms so obtained.

Extraction of liquid with one of the solvents already mentioned is often of assistance in this work, and adsorption on substances such as kaolin, tristearin, silica gel, aluminium hydroxide or cotton wool is now usual. The resulting columns may be examined in ultra-violet light before and after treatment with a reagent which produces fluorescence with one or more of the constituents of the mixture present, or which destroys any existing fluorescence. Alternatively, a fluorescing column may be used for the experiment and changes in the appearance due to the constituents present noted. However, these methods are chiefly applicable to organic substances, such as drugs and dyestuffs, and find few applications in sedimentary petrography.

SPECTROPHOTOMETERS

In recent years the use of the spectrophotometer for measuring both the wavelength and corresponding intensity of the bands of fluorescent substances has been greatly developed. Unfortunately,

instruments of this type are very costly and for most ordinary purposes they are not necessary. It is, however, of some importance as a rule to be able to measure the intensity of the fluorescence.

Instruments for this purpose are known as fluorimeters. They are usually of two main types, viz. the fluorescence is matched visually or by means of a photo-electric cell system. Thus the well-known Hilger-Spekker Photoelectric Absorptiometer¹ can now be obtained in a form which enables it to be used as a fluorimeter for liquid samples. E. J. Bowen² compared the merits and limitations of several types and makes some useful comments on general fluorimeter design. F. Wokes³ and co-workers have discussed generally calibration of fluorimeters. They point out that fluorescence measurements may give low results when the concentration is too high or too low, when too much ultra-violet radiation is reflected from the top or sides of the cell, when the solvents are impure, the pH incorrect, or when oxidation by gaseous oxygen occurs. To a considerable extent these errors can be overcome by correct instrument design and by special precautions, but it is best to calibrate with standardized solutions under conditions similar to those being used for the test.

Where pure materials are available, comparison standards can be made in the normal way, but it is sometimes convenient to use substances such as quinine sulphate, sodium fluorescein or other compounds which fluoresce in solution. However, for routine work in setting instruments, glass standards have proved very useful. M. H. Fletcher⁴ and co-workers described the preparation of glass standards for use in the analysis of beryllium; such standards, being permanent, should find wide use in quantitative work if the requisite degree of accuracy can be attained.

PHOTOGRAPHIC METHODS

These enter largely into many of the methods used, since it is important to be able to reproduce images of fluorescence phenomena. Photographic methods must, however, always suffer to some extent from the handicap that they are unable to reproduce colour effects faithfully, and in the case of fluorescence phenomena (which are characterized by very subtle differences in colour) this is a particularly adverse criticism. Good colour pictures can be obtained by use of the tri-colour films now commercially available (e.g. Kodachrome) as the author can confirm from his own experience.

¹ See Chapter IX, p. 393.

² *Analyst*, **72**, 1947, p. 377.

³ *Ibid.*, **69**, 1944, p. 1.

⁴ *Ind. Eng. Chem., Anal. Ed.*, **18**, 1946, pp. 179, 204.

It is necessary to distinguish between two types of such photography. In the first, fluorescent light emitted by the object, and in the second ultra-violet light reflected from the irradiated object, is all that is recorded on the plate (fluorescence photographs and ultra-violet light photographs, respectively). The whole subject is a very extensive one and can only be discussed very briefly here.

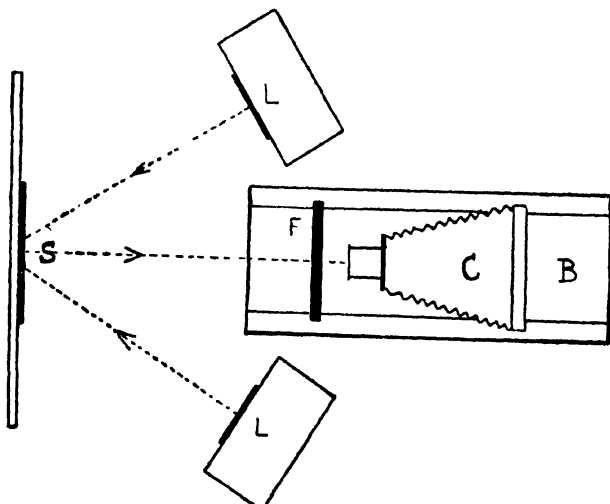


FIG. 66. Photographic Apparatus.
(Line drawing from J. A. Radley and J. Grant's 'Fluorescence Analysis in Ultra-Violet Light' (Chapman and Hall, London).

In order to photograph fluorescence, two filters are necessary, *viz.* one in front of the lamp, so that only ultra-violet light passes to the object, and one in front of the camera, to absorb any ultra-violet light which may be reflected, although it must transmit the visible light of the fluorescence. Wratten filters 18A and 2A, respectively, are suitable.

For ordinary routine work a simple apparatus (Fig. 66) can be easily set up and left as a permanent fixture in the dark-room. The camera C, which may be any type of view-camera, stands 75–100 cm. from the object clip, and its lens need not be of quartz (since it is not recording ultra-violet light). A glass-walled filter-cell containing cerium ammonium nitrate (see p. 440) is placed in front of the camera at F, B being an optical bench and LL sources of filtered ultra-violet light. If the object (S) has a flat surface, oblique

illumination is best, and if two lamps are available, as assumed in Fig. 66, one on each side will ensure uniform illumination and freedom from shadows. If the object is highly-reflecting, the lamp is placed at an angle of 45° to the line between the object and camera (CS) so that very little ultra-violet light is reflected to the camera.

Plates and exposure times are largely matters of personal experience, depending on the nature of the sample and fluorescence under examination. However, the literature contains many examples¹. Ultra-violet light photographs are seldom required in applications of this technique to sedimentary petrography.

FLUORESCENCE MICROSCOPY

This is one of the most interesting applications of fluorescence as a testing method. It depends on the use of ultra-violet light as a source of illumination for the ordinary microscope lamp. In this way many micro-structures are rendered visible by their characteristic fluorescence, just as in macro-work with the naked eye, observation in ultra-violet light discloses features which are normally invisible. Numerous applications of the method exist; some are referred to in later sections of this chapter. The method has recently been carried a stage further by the use of fluorescent substances as differential 'stains', and the 'secondary fluorescence' so produced frequently enables particular details of the structure to be picked out. This is an added facility, but it refers chiefly to botanical and biological samples.

The apparatus is not elaborate, but a good microscope is essential.

The other important factor is the source of ultra-violet light and in this connexion many proposals have been made. A spark discharge between cadmium or nickel-carbon electrodes has given good results when quartz, monochromatic microscope objectives are used. An arc-lamp with a copper-impregnated carbon electrode also gives an intense ultra-violet radiation. The principal difficulty seems to be one of intensity. Since a point-source is a considerable advantage, the usual form of mercury arc is far from ideal, although in certain designs radiations are concentrated as far as possible into one spot.

Filters and reflectors on the arc side should be made of some material which does not absorb ultra-violet light and, accordingly, ordinary optical glasses are eliminated. Quartz is best for converging lenses, condensers, etc., and it is an advantage although not essential, to replace glass mirrors by quartz prisms or silver reflectors.

¹ See J. A. Radley and J. Grant, *op. cit.* Bibliography, p. 462.

Filters to remove visible and infra-red rays, which mask the fluorescence and heat up both specimens and lenses, should also be inserted, so that the radiation eventually obtained covers a range of about 3,000Å to 4,000Å. Suitable filters are described above, a 10% solution of copper sulphate or cuprammonium solution in a quartz cell about 60 mm. thick being suitable for the purpose. Quartz is, however, not essential; any glass capable of transmitting ultra-violet light is suitable and less expensive. The copper sulphate should be pure, and the solution should contain a few drops of sulphuric acid and be renewed frequently. The slide should, of course, also be made of quartz.

For work in transmitted light, the cover-slip should preferably be opaque to ultra-violet light but transparent to visible radiation; this serves a double purpose of protecting the eye and of eliminating any fluorescence from the cement and lenses in the objective, which has been known to mask the fluorescence. Goggles to protect the eye from stray ultra-violet rays, or filters inserted in the eyepiece, are essential as a precaution against conjunctivitis.

If reflected light is used the cover-slip should obviously be transparent to both visible and ultra-violet light, and an ordinary glass slide may be employed if the ultra-violet light strikes the object from above only. Here again there are several devices for obtaining reflected light, a Lieberkuhn mirror being particularly efficient. Since a source of light of great intensity is required in such cases, this is best provided by a carbon arc, and this arrangement is also stated to minimize penetration of the ultra-violet light into the lens system. Comparison fluorescence microscopes for use with reflected light are now also available.

Extensions and refinements in the technique which, however, are seldom used in connexion with sedimentary petrography, are use of photographic methods and of 'stains' which selectively produce, destroy or alter fluorescence of the structures observed. These again are useful in biological and botanical work.

TITRATION EXPERIMENTS

In a number of methods it is necessary to carry out titrations from a burette in ultra-violet light. As the best results are obtained in a darkened room, the problem of reading the burette arises. Where the liquid is sulphuric acid (*e.g.* in titration of quinine), a few specks of quinine sprinkled on the surface will serve to show up the meniscus if a stray beam of ultra-violet light from the lamp strikes it. J. Grant¹ used a float consisting of a piece of glass tubing, about two-thirds of the diameter of the burette, which is two-thirds filled with

¹ *J. Sci. Inst.*, 9, 1932, p. 359.

a solution of quinine in dilute sulphuric acid containing a little oil as froth-killer, and sealed. The lower end may be drawn out to a point or weighted with lead-shot to keep the float vertical. The slightest illumination with ultra-violet light causes this to fluoresce brilliantly and to illuminate, not only the meniscus, but also the graduations, so that the burette may be read in the dark accurately to within 0.05 ml.

APPLICATIONS OF FLUORESCENCE ANALYSIS

Slags. A number of investigators have examined possibilities of ultra-violet rays for testing products of the silicate industry, and the results are fairly encouraging. Early workers investigated the appearance of iron blast-furnace slags under the lamp, and found that stable slags (*i.e.* those which do not disintegrate on storage) show a dark violet fluorescence on their freshly-broken surfaces. After weathering, yellowish-white spots appear on the violet background. Unstable slags, on the other hand, showed numerous clusters and spots of a red to yellow or a cinnamon-brown colour on the violet background. These brownish spots are attributed to particles of the γ -dicalcium silicate which are formed from the α - and β -forms with a corresponding 10% increase in volume.

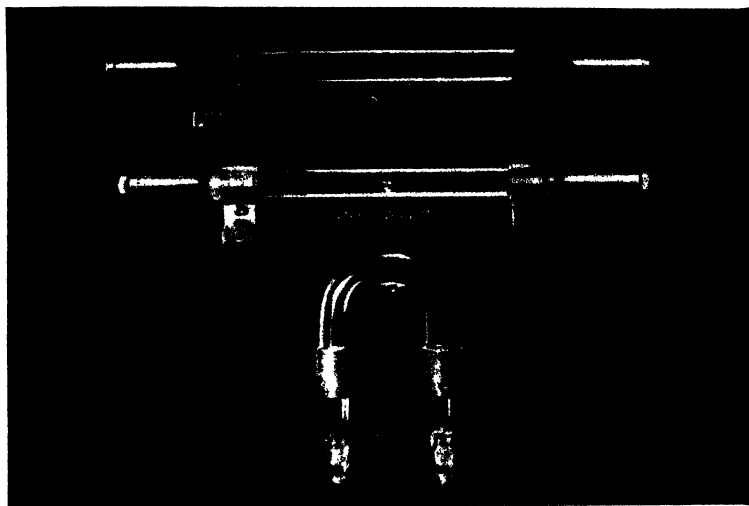
Basic slags do not normally fluoresce, but owing to the brown or vivid yellow fluorescence of raw phosphates (especially from Florida or Algeria), 10% of these are easily detectable in the slags. Extracts in water give unreliable results, but if 10% hydrochloric acid is substituted, the characteristic fluorescence is usually obtained. Extracts in ether or in alcohol are also strongly fluorescent, but this is usually due to presence of organic matter, *e.g.* lubricating oil derived from grinding processes.

The fluorescence microscope has been used to detect the presence of quartz in samples of dust after staining with auramine, which imparts a bright golden yellow colour to the quartz. An estimate of the amount present may be obtained by the use of a graduated standard slide. V. Kubelka¹ states that a number of road and track slags and slag cement do not fluoresce, but that Portland cement shows a light brown fluorescence. The fluorescence of pigmented cements is best studied in linseed oil pastes, but it is liable to be affected by the presence of calcium or barium sulphate.

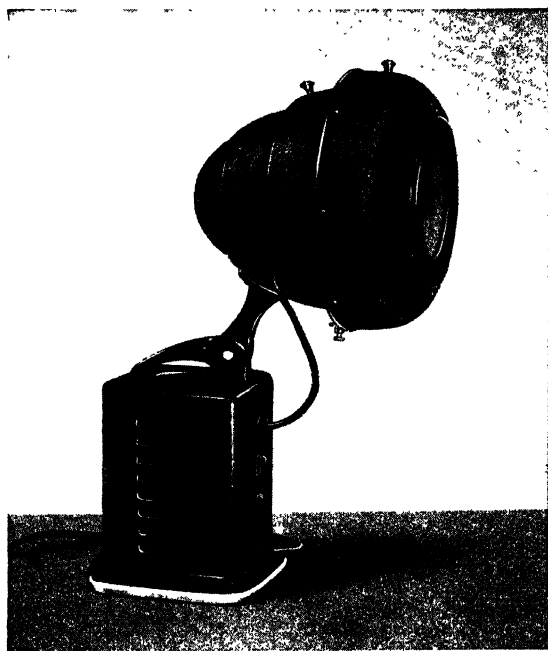
The weathering of rocks has been examined in ultra-violet light by A. Schmolzer² who tested specimens of stone taken from a church in Vienna. Small splits, cleavages and mica particles were easily visible under the lamp.

¹ *Chem. Listy*, 23, 1929, p. 337.

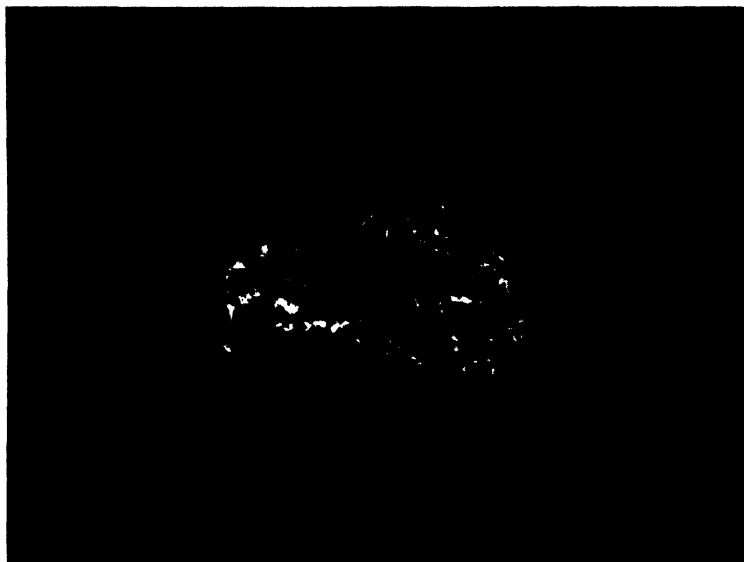
² *Stein-Industrie*, 12, 1927, p. 1.



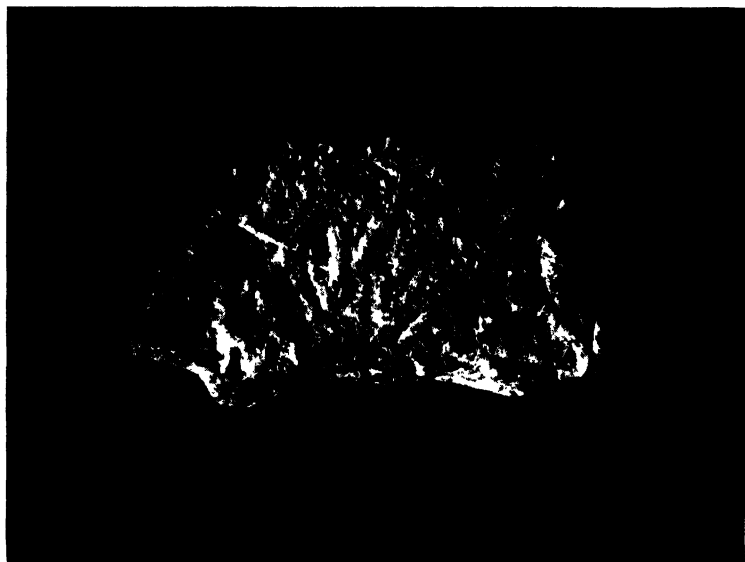
A. QUARTZ-MERCURY-VAPOUR LAMP BURNER.



B. HANOVIA LAMP MODEL XI
(Courtesy Hanovia Ltd.)



(i) UV light—Autunite shown as separate little patches.



(ii) Visible light—just a large blob of rock.

AUTUNITE DISSEMINATED IN PORPHYRY.
(From Foley Mountain, S. Dakota.)

(Courtesy J. A. Radley and J. Grant and Chapman & Hall Ltd., London.)

A method of investigating the degree of penetration of binding materials (such as bitumen in road carpets) and of stone-hardening preparations, is to saturate the rock with some fluorescent material such as a mineral oil and then to examine a broken face of the stone under the lamp. The penetrating material shows up brightly against the dull background of the stone and the amount of penetration may be easily gauged.

Portland pozzolana and other cement mixes may be graded in terms of strength by means of their fluorescence, comparisons being made against a standard colour-scale with the aid of a photo-electric cell. The method is in routine use in the U.S.S.R.

Mineral Fuels. In general, coal shows little of interest in ultra-violet light, but some bands of clarain have a golden speckled appearance, although the ash is without any characteristic fluorescence. Ankerite, which often occurs with coal, has a golden-yellow fluorescence.

The oil-shale group, however, gives more interesting results. Thus, common shales are dark brown in the massive state, although the colour may be absent from the powdered form. With a kerogen shale however, a rich chocolate-brown has been observed in both the powdered and the lump forms. Torbanite and cannel can be differentiated readily by their fluorescence, since the former shows bright yellow streaks on a brown background. F. Penta and L. Longo¹ treated samples of coal with 10% nitric acid and examined the acid extract. Lignite extracts fluoresced, the older coals usually red and the more recent coals green. Mineral coals gave non-fluorescent extracts. A sample of Cannel coal and one of Augen coal behaved like lignite, and a sample of anthracite behaved like mineral coal.

M. Wittich², who investigated Esthonian and Manchurian shale-oils, found that useful indications can be obtained as to their origin, preparation and process of cleaning, and that individual fractions can be graded according to their boiling-points from the fluorescence.

Traces of petroleum disseminated throughout a crystalline mineral give a brilliant and characteristic fluorescence. H. C. Dake and J. de Ment³ cite calcite crystals from several localities in Texas as examples.

F. B. Taylor⁴ considers that 1 part of petroleum oil per 100,000 parts of solvent is readily detectable by its fluorescence, and that the specific gravity of a crude oil is roughly indicated by its fluorescence colour. In water, heavy oils can be detected at a dilution

¹ *Boll. Soc. Naturalisti, Napoli*, **48**, 1937, p. 91.

² *Brennstoff-Chem.*, No. 19, 1927.

³ *Geophysics*, **12**, 1947, p. 72.

⁴ *Oil Weekly*, **106**, 1942, No. 2, p. 27.

of about 1 : 500,000, but petrol at only 1 : 20,000. Oil in soils is detectable at dilutions of 1 : 10.

When a well is drilled in any particular field, and samples from each of the various sands penetrated are tested and classified according to their respective fluorescent qualities, the record so obtained becomes an index for that field, because no two samples of crude oil exhibit an identical fluorescence unless they are obtained from identical sands. Samples from subsequent well-drillings may then be compared with the index and graded accordingly. Neither the gravity of the oil nor the percentage of mud and water in the sample interferes, and the sample may be obtained from a ditch or from bailings or extracted from the core if the formations are cored. J. de Ment¹ however, does not consider the method wholly reliable, since a number of factors may influence the results.

F. W. Bates² finds that, in general, a productive sand has a uniform fluorescence throughout, whilst a sand carrying salt water in addition to the oil has a mottled fluorescence. Methods of prospecting based on fluorescence characteristics of petroleum, have been devised; in all, personal judgement is an important factor.

Bitumens, etc. It does not appear to be possible to identify various bitumens in admixture with one another, even by examination of their solutions.

Several workers have studied coal tar, petroleum and stearin pitches, and crude montan wax. Each of these gives a characteristic fluorescence suitable for identification of the substance in the pure state, but not in admixture. It is advisable to work not only with solid materials, but also with their solutions in chloroform, or benzene; the latter may be allowed to evaporate on filter-papers, and the residue examined in ultra-violet light (see below).

Yellow fluorescent spots or patches due to anthracene are plainly visible in tar macadam preparations containing this compound, and J. Grant has found that its presence may be confirmed by removing it by controlled sublimation and testing the sublimate. Ukrainian anthracene may be distinguished from Siberian anthracene by the very weak fluorescence of the former.

The fluorescence method has been used for some years by H. B. Milner for detection and differentiation of bitumens. The general procedure adopted is to compare the fluorescence of an 0.5% solution (weight/volume) of the bitumen in carbon disulphide with a series of standards of equal concentration. Residual bitumens give bright, greenish-yellow fluorescences, quite distinct from the dull greenish-browns of oxidized bitumens, while asphaltic limestones

¹ *Mineralogist*, 13, 1945, p. 425.

² Quoted by J. de Ment, *loc. cit.*

give much yellower fluorescences than the residual bitumens. Trinidad Lake asphalt, Cuban asphalt and Gilsonite also have distinctive fluorescence colours.

Differences in fluorescence of bitumens are most apparent when the meniscus of the solution is studied, and in this way comparatively small variations may be detected. The visual method is, however, difficult to apply to the examination of mixtures; possibly a spectrographic or photographic technique would be more successful.

An 0.5% solution gives the best results, as differences become less marked with any increase or decrease in concentration. With substances containing mineral matter, the soluble bitumen content is first determined and a solution prepared of the requisite concentration. It is unnecessary to filter it if the solution is allowed to stand before examination of the fluorescence, as the mineral matter has no effect on the colour of the meniscus. Unfortunately standard solutions of different types of bitumen cannot be preserved without alteration of the fluorescence, even when sealed in glass tubes and kept in the dark. The change in colour of the fluorescence is most marked in the first few days, although thereafter little further change is apparent.

An alternative technique is to allow a drop of an 0.5% bitumen solution, free from mineral matter, to evaporate on a filter paper under the ultra-violet lamp, when the yellowish fluorescence seen initially gives place to a characteristic yellowish-white rim surrounding a brownish spot.

H. B. Milner's methods have not been extended to examination of the mixtures used in road-making. From the analytical point of view, unknown mixtures are likely to present considerable difficulty in identification. The fluorescence, for instance, of Trinidad Lake asphalt could be profoundly modified by the addition of flux oil, the exact effect depending on the source of the flux oil. Without a knowledge of all the ingredients, it is doubtful whether even a qualitative analysis of the mixture could be carried out by ultra-violet ray analysis.

Attempts have been made by other workers to apply ultra-violet analysis to the quantitative examination of unknown mixtures, such as determination of tar in tar-bitumen mixtures. H. B. Milner's experience is that the method may lead to serious inaccuracies for the reasons already stated. Tar-bitumen mixtures containing the same percentage of tar may have widely different fluorescences according to the type of tar incorporated, since, although tars have a much stronger fluorescence than asphaltic bitumens, their colour and intensity vary considerably. Horizontal retort-, vertical retort-, and oil-gas-tars are usually easily distinguished, although borderline cases occur where the distinctions are not so obvious. Removal

(by filtration) of the free carbon increases intensity of the fluorescence, but does not impair to any great extent distinctions between different types of tar.

The fluorescence colours of solutions of bitumens may be matched against those of calibrated standards consisting of solutions of appropriate dyestuffs in alcohol or benzene. It should be noted that fluorescence of bitumen is dependent to some extent on temperature and that this dependence is reversible.

D. M. Wilson¹ described tests to decide whether a mastic asphalt has been made from good asphalt rock or whether it has been 'enriched' by added bitumen, as such mastics are inferior to the natural product. The residue after extraction of the bitumen with a suitable solvent, is examined under the lamp. St. Jean rock has a pale sandy fluorescence; Sicilian and Val de Travers rocks a rather darker colour; crystalline limestone is dark brown; 20% of the limestone in St. Jean rock is readily detected. The colour of low-grade Seyssel rock asphalt is similar to that of the associated crystalline limestone, but can be distinguished under the fluorescence microscope since it appears reddish-brown in colour, whereas the crystalline limestone is bright crimson.

The presence of bitumen or petroleum in ores or rock is readily detected by sprinkling the powdered material on the surface of a suitable solvent under the lamp. The particles containing the hydrocarbons leave fluorescent streamers behind them as they sink.

In the examination of bitumens by paper strip chromatography, the light oil fractions gave cream to golden-yellow zones; tars gave orange, red-brown and brown zones, depending on concentration and molecular weight; asphaltenes gave dark brown or black zones.

W. Teuscher² states that 1 part in 50,000 parts of coal-tar pitch, which has a greenish-blue fluorescence, is detectable in asphalt (petroleum pitch) which fluoresces with a redder shade. The method is not suitable, however, for detection of asphalt in the pitch. Solutions of pitch or bitumen, and mixtures of the two in an inert solvent such as benzene or acetone, can also be differentiated in ultra-violet light. W. Becker³ claims to be able to estimate the components of the mixture of tar and bitumen rapidly and with an error of 5%. The samples are dissolved in petroleum spirit, and the colours are compared under the lamp with those from the standard mixtures of known compositions. Paraffin oil, which normally does not fluoresce, appears blue if more than 5% of petroleum (spirit or jelly) is present. Crude oils of German origin have a yellow

¹ *Contract Journ.*, 1935, May 1st.

² *Chem.-Fabrik.*, 54, 1930, p. 987.

³ *Ashphalt u. Teer*, 30, 1930, p. 87.

or brown fluorescence when spotted on filter-papers, while refined oils develop a light blue colour. Light oils containing benzene also appear yellow, but when the benzene and asphaltenes are removed, this turns progressively brown, and eventually all fluorescence vanishes.

Minerals. The behaviour of these substances in ultra-violet light depends to a very great extent on source of origin; on the colour of the sample itself; and on the presence of small traces of compounds which often modify or actually produce the fluorescence.

J. de Ment¹ has listed the response of many minerals to short- and long-wave ultra-violet and cathode rays, and their thermo- and tribo-luminescence behaviour. Discrepancies in results of various workers arise owing to differences in the light source used for excitation. Some minerals are inert to short wavelengths, and *vice versa*. Most transparent minerals may be phosphor bases, and would fluoresce providing certain activating elements are present in solid solution in amounts close to the optimum for fluorescence. Certain elements also act as quenchers. The fluorescence of minerals is seldom sufficiently characteristic to serve as a means of identification except in certain cases mentioned below, but variation in fluorescence of several samples of the same mineral from different localities may be of some use for sorting of samples for collections.

The rare earth oxides seldom show any fluorescence in ultra-violet light, although certain inherent rare earths may modify fluorescence of the fluorites. The natural carbonates, witherite, strontianite and barytolcalcite can show strong fluorescence. Glauberite from Chili had no fluorescence, but those from Borax Lake, in California, and from Laramie, glowed vividly. With pectolite a fluorescence was obtained even from specimens that had almost completely changed over to steatite, and a fluorescence was also obtained with wollastonite. Cerussite in unfiltered light appeared greenish-yellow to apple-green, although in the filtered light the fluorescence colours varied from sulphur-yellow to pale violet. Pure artificial lead carbonate has no fluorescence.

Calcium Minerals. The fluorescence of samples of gypsum from Sicily has been found to be from two to five times as intense as that of samples from Bavaria and elsewhere, and J. Grant has also noted different shades of red and violet in samples ('mineral white' or 'pearl hardening') submitted for use in paper manufacture. It is not certain that these can be completely related to the source of the mineral. After exposure to radioactive radiations, calcium sulphate containing about 0.001% of thallium has a red fluorescence at low temperatures.

¹ See Bibliography, p. 462.

W. Witteborg¹ and A. Josten², however, examined calcite minerals rather from the point of view of faults in crystal structure, and the former claimed to be able to demonstrate comparative ages in this way. Similarly, A. Josten³ found that ultra-violet light renders the 'sundial' structure much more apparent, and he considers that the fluorescence may be due to a foreign substance which is segregated in the direction of crystal growth. In this connection, H. Yagoda⁴ has used the photomicrography of fluorescent, polished, mineral sections as an aid to their identification and to emphasize contrasts in structure.

Although the fluorescence of calcite varies, it is best excited by the ray 2,537Å, and it is then generally pink to deep red in colour, although some American and German specimens are yellow to green. Calcites from Lovington, New Mexico, and Ritter Hot Springs, Oregon, often fluoresce pale green, whilst those from Arizona and Texas and other localities fluoresce blue. M. Déribéré⁵ noted that an aragonite from Girgenti had a rose colour in the fibrous radial parts and a blue-green fluorescence in other portions, with a very fugitive green phosphorescence. H. Haberlandt⁶ found that several calcites from different sources contained porphyrins affecting the fluorescence, whose presence he ascribed to bacterial action.

M. Déribéré⁷ records that a very persistent fluorescence occurs in some natural calcium compounds. Thus fragments of stalactites and stalagmites were found to continue to fluoresce visibly for periods of up to 7 seconds after removal of the exciting source. This may, in fact, be regarded as a form of phosphorescence. The intensity of the fluorescence falls gradually during this period, this decrease often being associated with loss of occluded water. The presence of silica is without influence on the phenomenon, but traces of iron (e.g., 0.5% to 1% as Fe_2O_3) inhibit it. The red-orange fluorescence of certain manganiferous calcites increases with the manganese carbonate content, reaching a maximum at 3.5%, and disappearing at 17%. The fluorescence colours of certain calcites change when fresh surfaces are cut.

Felspars. Certain types of natural silicates, such as potassium feldspars, potassium-sodium feldspar and datalite, have a blue fluorescence, the activator being traces of europium. Potassium feldspars

¹ *Zentr. Min. Geol. Paläont.*, 1932, p. 364.

² *Ibid.*, 1930, p. 432.

³ *Loc. cit.*

⁴ *Econ. Geol.*, 41, 1946, p. 813.

⁵ *Ann. Soc. Geol. Belg.*, 65, 1942, p. 272.

⁶ *Naturwiss.*, 27, 1939, p. 613.

⁷ *Compt. rend.*, 207, 1938, p. 222.

of granitic-syenitic origin are particularly fluorescent, but pegmatitic feldspar is inert. Pegmatitic type potassium-sodium feldspar, however, does fluoresce. The greatest degree of fluorescence is shown by plagioclases containing 30 to 40% of anorthite (andesine), and andesine which contains a little strontium and lead, is highly fluorescent. A. Kohler¹ used the fact that a feldspar melt is extremely sensitive to traces of europium and cerium, developing a blue fluorescence in their presence, to detect the presence of the two elements in many other minerals. Thus he powdered them and introduced them into a fused, non-fluorescent feldspar.

Some autunites fluoresce with the typical uranium colour, although other specimens do not. Pl. 17 shows how autunite disseminated in Dakota porphyry may be rendered visible. There appear to be two minerals present in autunite, both of which fluoresce, but with an orange and lemon-yellow colour, respectively. A specimen of hyalite in a trachytic rock from Mexico fluoresced with an intense green colour, but no other sample of hyalite did so. A vein of willemite in franklinite may be rendered visible by means of its green fluorescence; if a filter is used which transmits this ray but cuts out fluorescence due to other inclusions.

The quantitative relationship between the fluorescence of scheelite and its molybdenum activator content holds true for the natural minerals of the isomorphous scheelite-powellite series and for synthesized specimens of the isomorphous calcium tungstomolybdate series. The fluorescence of powdered calcium tungstate is bright blue if traces of molybdenum are present, but a paler blue and neutral white when the molybdenum content reaches approximately 0.5%. As the molybdenum content rises the fluorescence colour becomes increasingly yellow, and reaches a maximum intensity at 4.8% molybdenum, above which its colour also is almost unchanged. Quantitative results obtained from a comparison of fluorescence colour and intensity against standards agreed closely with those obtained by chemical analysis.

Fluorites. Most of the pioneer work on these minerals is associated with H. Haberlandt², who noted red zones or specks in the fluorescence of fluorites from various parts of Germany. No spectral lines corresponding with rare earth elements could be detected; and since the specimens showing the natural red fluorescence came from radioactive regions, it was concluded that this colour was of the same origin as that of the artificially irradiated fluorites. Rare elements or bituminous impurities may also account for the nature of the fluorescence observed. H. Haberlandt's experiments with

¹ *Z. Krist. Min. Pet.*, 52, 1940, p. 272.

² *Nature*, 133, 1934, p. 99.

synthetic fluorites (*i.e.* calcium fluoride containing 0.1% of rare earths), showed that europium is probably responsible for the blue, and ytterbium for the green component. K. Przibram¹ found that when europium oxalate is heated with calcium chloride, the resulting product had a fluorescence similar to that of certain fluorites, and he therefore suggests that fluorites contain traces of divalent europium.

Uranium Minerals. J. de Ment² has dealt in detail with the fluorescence of uranium minerals and the various fluoro-chemical tests for them. As a rule the primary uranium minerals do not fluoresce brightly but the secondary minerals do. Pitchblende and carnotite are non-fluorescent, but their altered products (such as zippeite) fluoresce bright yellow or green. Uranophane, uranospathite, dakeite and uranium phosphates are almost invariably fluorescent. The non-fluorescent uranium minerals include the silicates and uranium micas, $M_2(VO_2)_2(ZO_4)_2$, with 8 or 12 molecules of water, in which *M* is Ba, Ca, Mn, Cu, Fe, etc., and *Z* is P or As. All the uranium micas fluoresce intensely after fusion with sodium fluoride. Uranium phosphates, arsenates and sulphates have an intense yellow-green fluorescence, and the carbonates have an intense green when no interfering cations are present.

Willemite. Fluorescence of willemite varies according to the source and although fluorescence is not a sure test as to presence or otherwise of willemite, the method has been used for examination of tailings of the crushed ore. That the fluorescence colour of willemite is not related to the colouring of the crystal, is shown by the fact that some colourless crystals gave a rich violet fluorescence, and that often the coloured specimens show no fluorescence at all. Artificial willemite does not fluoresce when pure, but addition of an alkali or of a trace of manganese induces the phenomenon.

A pale green cleavage slab of willemite from Franklin Furnace gave a brilliant uranium-green fluorescence, followed by phosphorescence. Another sample from the same locality had pale green willemite grains embedded in a cleavage mass of white calcite, the resultant effect being a flesh-coloured, dark red mass with a number of brilliant green fluorescent spots (Pl. 18). Samples of the red radiating willemite (which form the base of the colourless crystals from Broken Hill) fluoresced with a bright yellow colour although only in patches. The significant conclusion to be drawn from these results is the dependence of the fluorescence of willemite on the content of its minor constituents.

¹ *Nature*, **141**, 1938, p. 1,113.

² *Mining Congress Journ.*, 1945, Jan.

L. Royer¹ found that anglesite has a fluorescence similar to, though distinguishable from, that of galena; it is also possible to differentiate anthracitic and graphitic from bituminous and carboniferous rocks. Neither opal nor the particular sample of willemitite examined by L. Royer fluoresced immediately in ultra-violet light, but the former did so after exposure for a few minutes. F. R. van Horn² concluded that the degree of weathering exerts a potent influence on the nature and intensity of the colours observed, and the presence of radioactive elements also produces variable results. The strategic importance of scheelite has intensified prospecting for this mineral, and cold arc tubes in portable apparatus are widely used in this work for detecting and identifying outcrops or pieces of this species. Fluorescence methods are also used in sorting these and other ores as they move along a conveyor belt, and to inspect mill-tailings in extraction processes.

Gems. The same general considerations apply as with minerals. Some early work using the fluorescence microscope was carried out by A. von Loehr³ and G. Riedl⁴ introduced the use of colour filters to obtain a rough classification of the fluorescent light, also to eliminate the colour of the gem itself. Much interesting information on the behaviour of gems in ultra-violet light, cathode rays and X-rays is given by G. Riedl.

A strong orange-yellow fluorescence is given by colourless or white natural sapphires, but artificial sapphires often have a pale reddish fluorescence, probably due to chromium oxide. Yellow sapphires can be differentiated from all other stones by their striking orange-yellow colours. A much weaker but more yellow fluorescence is shown by yellow topaz; these are the only yellow stones which fluoresce. Dark blue sapphires have practically no fluorescence, and the brighter forms show variations in intensity when viewed through colour filters. The best differentiation is obtained with Ceylon and Montana sapphires; the Australian and Indian stones react only weakly. The fluorescence of artificial blue sapphires is moderately strong and reddish-violet in colour. Artificial blue spinel fluoresces with a strong red colour, and a greenish to yellow fluorescence is usually shown by blue topaz.

Siam rubies may usually be differentiated from Burmese and synthetic rubies by their much weaker fluorescence. The pale purple variety of Ceylon rubies shows up strongly through a red filter, the fluorescence being often similar in intensity to that of Burmese rubies. Little or no fluorescence is observed with red

¹ *Bull. Soc. Franc. Min.*, 53, 1930, p. 515.

² *Amer. Mineralogist*, 15, 1930, p. 461.

³ *Min. Petr. Mitt.*, 31, 1912, p. 35.

⁴ See ref. 1, p. 440.

zircon or with red beryl, garnets or tourmaline. The fluorescence spectrum of the ruby is similar to that of the sapphire.

The following notes are selected from tests made by J. Grant¹ on authentic samples representing 30 different types of precious and semi-precious stones, and the examples given below are intended to show how the method may be of use to distinguish stones which (except to the expert) appear alike.

A synthetic aquamarine is sometimes confused with genuine Burma sapphire, but may be distinguished by its dull pink fluorescence, the latter stone appearing dark purple or black, and in this respect indistinguishable from the synthetic sapphire.

White topaz, white zircon and diamond also appear alike in daylight, but have a dull purple, pale mustard-yellow, and mauve to black fluorescence, respectively. The method fails to distinguish diamond from paste, but true diamonds show various shades of purple or mauve, presumably according to the method of cutting used.

Opal ('whiteclaffe') has a fluorescence similar in colour to that of an egg-shell, the characteristic green fire and orange-yellow colour seen in daylight, being invisible; this easily distinguishes it from moss agate, which is grey with a blue streak. Black opals have no fluorescence, and Mexican fire opals appear dull purple, but each of these stones is easily recognized by the unaided eye.

Chinese jade, amazonite, soudée emerald (beryl type) and chrysoprase also resemble one another, and the fluorescence effects, though similar, are distinguishable, being dark green with bright streaks, dirty pale green, very dark green, and pale opalescent green, respectively. Newly cut jade has, however, a different fluorescence from that of old jade. The brilliant, fiery deep-red fluorescence of the synthetic ruby readily distinguishes it from the paler and more pinkish red of the genuine ruby.

Other fluorescence colours which may be of interest (although the stones concerned are easily recognized without their aid) are as follows: genuine and imitation amethyst, mauve to black and mustard-yellow, respectively; blue and yellow sapphire, pink and orange, respectively; red and blue zircon, dirty red and dirty yellow, respectively; yellow and white topaz, dirty yellow-brown and dull purple respectively; peridot, garnet, carnelian and turquoise, dark brown-green, dull purple, dull purple and mouse-grey, respectively.

Diamonds have naturally received much attention and many specimens fluoresce, usually blue, but sometimes green, orange, orange-yellow, brown or red shades or not at all, often according to origin. H. C. Dake² noted that his blue fluorescent samples contained an unusually high proportion of chromium and the yellow fluorescent samples an unusually high proportion of

¹ *Analyst*, 62, 1937, p. 731.

² *Gemmologist*, 11, 1942, p. 55.

aluminium, whilst his non-fluorescing samples had no preponderance of any foreign element when examined spectroscopically.

In the so-called 'zone fluorescence' of some diamonds a distinct band of fluorescence of one colour completely surrounds a central area having quite a different fluorescence colour, the effect being best observed on cleavage faces. Blue fluorescent diamonds do not generally behave thus, and yellow fluorescent samples show numerous parallel bright streaks. The use of ultra-violet light in a rather different way enables diamonds to be divided into two classes. The first comprises the commoner forms of diamond which are opaque both to infra-red and ultra-violet rays and have a uniform blue fluorescence. The second class is relatively rare, and is transparent to those radiations and non-fluorescent.

Pearls. It is not so much the difference in the colour of the fluorescence that assists differentiation between culture and artificial pearls, as the difference in transparency to ultra-violet light. Thus, if the pearl is placed on a photographic plate under the lamp, then in the case of the culture pearl the image obtained is of uniform intensity, whilst that from a genuine pearl shows dark and light patches. No actual fluorescence is shown by artificial pearls unless they contain uranium compounds as a colouring agent, since the other metallic compounds used as colourings do not fluoresce under the lamp.

Mother-of-Pearl. Living *Trochus*, *Monodonta*, *Cantharidus*, *Haliotis*, *Padollus*, *Gena*, *Nucula*, *Trigonia*, *Meleagrina*, *Multela*, *Unio*, *Nautilus* and *Spirula* usually show a blue-white or mauve to violet fluorescence. With fossil *Nautilus* and other types, the fluorescence is usually yellow, orange, or dark red, i.e. the same as shown by a calcareous sediment, indicating that the shell has been altered. Some fossilized *Trigonia bronni* and *Nautilus umbilicaris* however, have a blue to violet fluorescence colour.

Small amounts of organic remains incorporated in stones or fossils often fluoresce under the lamp, and photography in ultra-violet light can reveal much greater detail. The structure of many fossils has been examined in this way, and imitations and hidden repairs are often clearly visible. The original sutures of bones which appear to be single, but which are really compound, are also revealed. The fossils to be photographed should be quite free from dust, blemishes and finger-prints, all of which can appear in the finished picture. A filter consisting of a thin cell with parallel sides 1 cm. in thickness and containing a 1% solution of cerium ammonium nitrate, or an Ilford Q filter, should be placed between the camera and the object. This is necessary in order to absorb any ultra-violet reflected from the object which would fog the photograph (see p.

445, and Fig. 66). K. Portratz and H. Ziegenspeck¹ found the fluorescence microscope of value for investigation of fossils in peat.

In some prehistoric dwellings at Wisternitz, a mammoth's tusk was found, carved to depict a woman, and it was possible to show with the assistance of the lamp that the specimen was the untouched work of a carver of the immediate post-glacial period.

Burned bones do not fluoresce, although old unburnt bones fluoresce brilliantly. In this way it was possible to prove that certain bones found in a Dutch megalithic tomb owed their colour to age and had not been heated. P. E. Spielmann² applied the method to bitumen used for embalming.

The peculiar fluorescence of the shells of gastropods (e.g., the families *Trochidae* and *Turbinidae*) appears to offer a useful means for detection of the presence of certain pigments, even when these are overlaid with other colouring matters.

Old marble fluoresces in a mottled white, or white with yellow and blue tones, whereas the surface of freshly-cut marble appears a uniformly intense purple. Before examination, the surface of old marble should be cleaned carefully with distilled water in order to remove organic or other matters which may fluoresce or otherwise confuse results. Thus G. M. A. Richter³ examined the statue of Diogenes in the Metropolitan Museum (New York), and concluded from the mottled appearance of the base and the lower portions that these only are of ancient origin, the upper portion being of more recent date.

Alabaster and limestone objects also show similar ageing phenomena to marble, but it is more difficult to correlate the extent of the change with the age. Very old and thin-walled objects in alabaster show ageing throughout the entire thickness, and in such cases there is a tendency for breaks to exhibit the same white fluorescence as the original surfaces. The methods can detect additions or restorations made with plaster, with ground stone in the form of cement, or with new portions cut from actual stone, owing to the differences in the fluorescence between the old and the new portions.

Loadings and Pigments. J. Grant examined a large number of mineral loadings used in paper making, and was able to distinguish good china clay (weak violet) from mineral white (bright violet), talc (weak blue-grey), blanc-fixe (strong blue-violet), and chalk (brighter blue). Chalk, zinc sulphide and zinc oxide were found to vary in appearance according to their degrees of purity, but the grades

¹ *Blatt. Unters. u. Forsch. Inst.*, 6, 1932, p. 6.

² *J. Egypt. Archaeol.*, 1932, Nov.

³ *Metropolitan Museum Studies*, 2, 1929, p. 29.

of titanium oxides could not be distinguished either from one another or from china clay. The method is very useful for checking deliveries, and in one instance this author was able to detect tinting dyes added to china clay.

Some results obtained by examination of a number of mineral pigments are given below, but care must be taken in drawing conclusions, as the presence of small amounts of impurities (e.g. in samples from different sources) produces far-reaching effects on the colour of the fluorescence.

PIGMENT	FLUORESCENCE COLOUR
Ground Shale	Dark blue
Fixed White	Fairly strong violet
Light spar	Fairly strong violet
Precipitated chalk	Black
Ground chalk	Red with brownish tinge
Natural chalk	Dark yellow
Siliceous chalk	Fairly strong red-violet
Kaolin	Deep reddish-violet
Talcum	Dirty red-violet
Pure cinnabar	Dark
Cinnabar substitute (Lithol red)	Cinnabar-red
Cinnabar substitute (Permanent red)	Carmine
Pure red lead	Dark
Red lead substitute (Lack red)	Orange-red
Red lead substitute (Helio orange)	Reddish-brown
Zinc yellow (zinc chromate, pure)	Dark
Zinc sulphide	Orange
Magnesium oxide	Blue-green
Magnesium carbonate	Violet

To sum up, it is apparent that fluorescence analysis in ultra-violet light offers a wide range of techniques applicable in sedimentary petrography. However, in most cases these must be used with discrimination, and usually on the basis of comparison with materials of known origin and composition. Indeed the methods of fluorescence analysis will usually serve to supplement existing chemical and physical methods rather than to replace them.

Future developments are likely to be concerned chiefly with measuring fluorescence numerically, so as to obtain quantitative results wherever possible, and with development of the technique of fluorescence chromatography. Fluorescence microscopy also offers wide scope in its applications to sedimentary petrography.

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CHAPTER XIII

X-RAYS AND THEIR APPLICATION TO MINERAL ANALYSIS

A. E. Kiss, B.SC., A.INST.P.

Crystal Morphology and the Atomic Lattice—Atomic Planes—Production of X-Rays—Radiation from Targets—Interaction of X-Rays with Matter—Monochromatization by Filters—Fluorescence—Photographic Effect—Ionization of Gases—X-ray Counters—Diffraction of X-Rays by Crystals—The Bragg X-Ray Spectrometer—Crystal Monochromator—X-Ray Diffraction Techniques and their Interpretation—The Debye-Scherrer Powder Method—The 19 cm. Powder Camera—Small Angle Diffraction—Film Measurement—Accuracy of Plane Spacing Measurements—Powder Specimens—Interpretation of Powder Diagrams—Cubic Crystals—Crystals of Lower Symmetry—Single Crystal Methods—Unit Cell Dimensions—Single Crystal Specimens and Apparatus—Atomic Configurations—The Laue Photograph—Orientation of Crystals—X-Rays and Mineral Structure—Atomic Structure of Minerals—Mineral Identification: X-Ray Absorption—X-Ray Spectrum Analysis—Mineral Identification by Powder Diagram—Identification of Mixtures—Quantitative Analysis of Mixtures—Mixed Crystals—New Minerals—Particle Size Analysis—Geological Processes—Selected Bibliography.

CRYSTAL MORPHOLOGY AND THE ATOMIC LATTICE

LONG before the advent of x-ray methods, observation of crystal habits showed that facets formed on a given substance were always to be found in the same relative orientation, and related to one of seven geometrical forms based on the parallelepiped and the regular hexagonal prism, the axes of which could be assigned definite directions within the crystal. Many physical properties such as thermal and electrical conductivities, refractive indices, optic axes, cleavage, hardness and magnetic susceptibility, were found to be related to these axes.

The morphology shown by crystalline solids results directly from the precise and repetitive packing of atoms and molecules. The

atoms and molecules are found to occur in identical groups of one or more, these groups being arranged in three dimensions much as the units of a wallpaper pattern. The crystallographic axes are chosen so that, along them, these groups repeat at regular intervals (the repeat distance) in as simple a manner as possible.

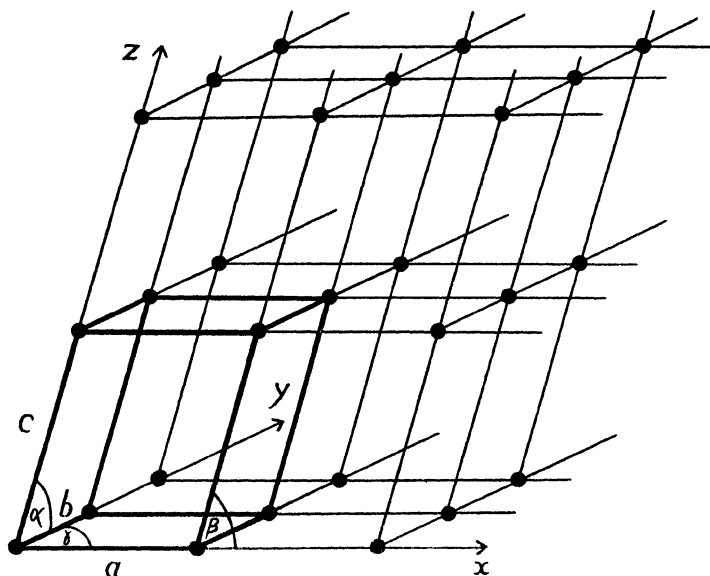


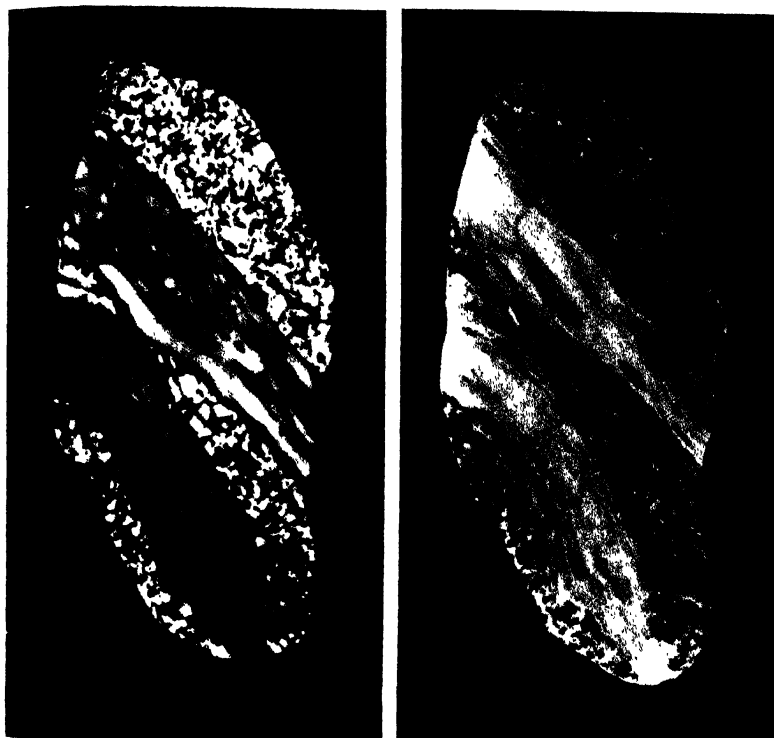
FIG. 67. The Atomic Lattice and Unit Cell.

An imaginary scaffolding, the space lattice, consisting of three sets of regularly spaced straight lines parallel to the three axes, may be constructed (Fig. 67), points of intersection of which, along these axes, give the repeat distance in that direction even when so chosen that in fact no atoms occupy these intersections.

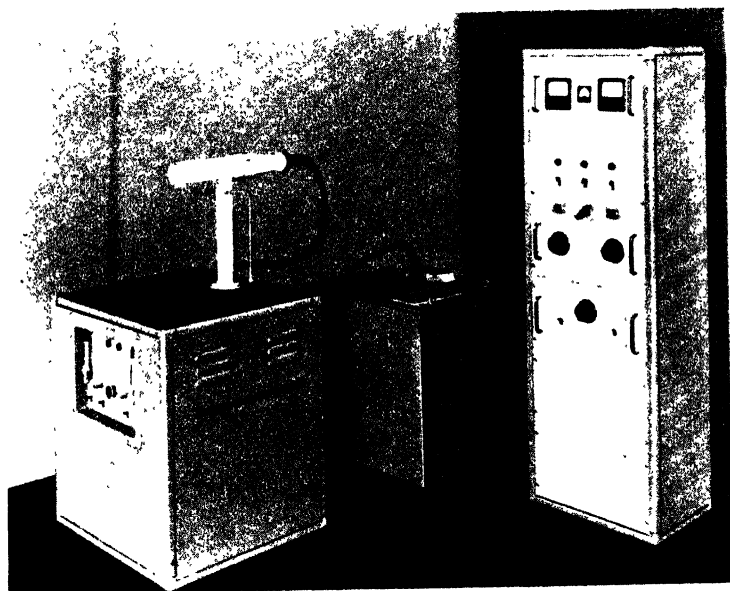
The unit cell is the smallest parallelepiped (heavy lines, Fig. 67), whose contents, repeated identically at intervals of a , b , c , along the x , y , z axes respectively, build up the entire structure.

Based on the relative dimensions and angles of this unit cell, A. Bravais distinguished six different forms which, together with a right hexagonal prism, were sufficient to represent all crystal lattices and which are called cubic (isometric), tetragonal, hexagonal, rhombohedral, orthorhombic, monoclinic and triclinic.¹

¹ See also Vol. II, Ch. I.



CLEAVAGE SLAB OF WILLIMITE.
(Franklin Furnace).
Left, Ultraviolet light. *Right*, Visible light.
(Courtesy *J. Grant*.)



THE RAYMAX 60 X-RAY GENERATING PLANT.

(Courtesy Associated Electrical Industries Ltd., London, W.C.2, and Newton Victor Ltd., London, W.C.2)

ATOMIC PLANES

Fig. 68 shows an extensive atomic pattern in two dimensions. The atoms can be seen to lie in rows; all the atoms may be accommodated on any one of the set of row lines drawn, each such set of rows having a perpendicular spacing d and orientation to the axes governed by the unit cell geometry.

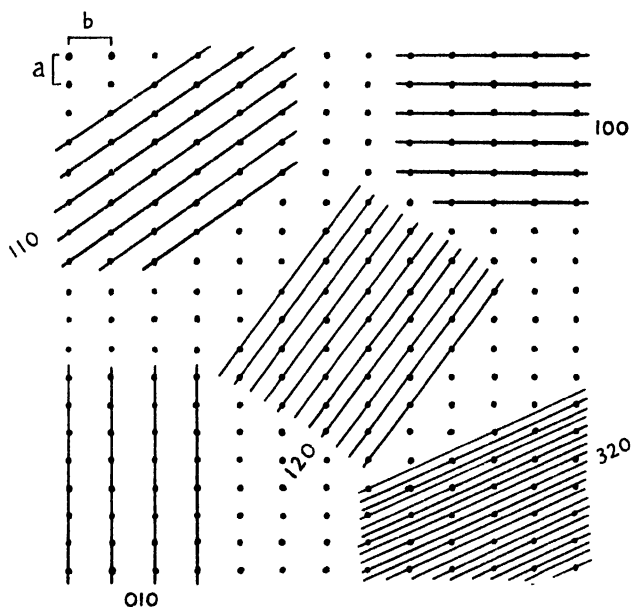


FIG. 68. Various Sets of Planes in a Crystal.
(After C. W. Bunn, *Chemical Crystallography*.)

Miller Indices

To identify a particular set of row lines, integral indices introduced by Miller are used. In Fig. 68 rows (320) divide the repeat distance a into three equal parts and b into two equal parts. The Miller indices (h, k) for these rows are (3, 2), and are inversely proportional to the lengths of the intercepts made by adjacent rows on the axes, where the units of length used are a and b respectively. This inverse relationship simplifies the Miller indices for row lines parallel to the axes, h being 0 for row lines parallel to the a axis, since the intercept is infinite. In three dimensions the atoms form sets of

parallel 'net planes', each set identified by Miller indices (h, k, l) derived by an extension of the foregoing procedure, with an interplanar spacing d_{hkl} .

Inspection of Fig. 68 reveals that planes of small Miller indices have the largest spacings and the greatest areal density of atoms. It is from such planes that crystal faces generally arise, demonstrating clearly the origin of the Law of Rational Indices. Cleavage properties depend on the atomic constitution of the planes, an interesting discussion of which is given by W. A. Wooster¹.

PRODUCTION OF X-RAYS

X-rays were discovered by Roentgen in 1895. Early experiments established that the rays originated from those parts of a gas discharge tube upon which cathode rays (electrons) impinged. The bombardment of suitable solids by high speed electrons forms the general basis for controlled production of x-rays in the laboratory, a large proportion of modern plant using the Coolidge or vacuum tube apparatus (Fig. 69).

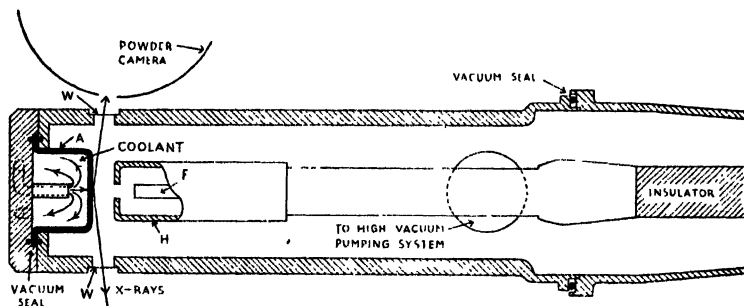


FIG. 69. Raymax 60 Demountable High Vacuum X-Ray Tube Assembly.

(Based on information supplied by Newton Victor, Ltd.)

Electrons are produced within an evacuated tube by thermionic emission from an electrically heated tungsten filament F and accelerated to large velocities by means of a potential difference, V , maintained between filament and anode (or target), A . The focusing hood H concentrates the electron stream on to a small area of the target where only a small fraction (about 0.2% for a copper target at 30,000 volts) of the energy imparted to the electrons appears as x-rays; the remainder is dissipated as heat in the target which is therefore continuously water-cooled.

¹ *Crystal Physics*, (Cambridge University Press), 1938.

X-rays generated at the surface of the target are permitted to leave the apparatus through one or more windows *W* relatively transparent to the rays. Thin, non-porous foils of light elements such as aluminium and beryllium are commonly used, the minimum thickness being governed by the necessity to withstand the inward pressure of the atmosphere when the tube is evacuated.

The x-ray beam intensity depends on the tube current, control of which is provided by varying the filament temperature. Pl. 19 shows a modern demountable x-ray apparatus suitable for crystallographic work, in which both filament and target are readily replaced. The tube is continuously evacuated during use by an oil diffusion pump backed by a rotary mechanical pump.

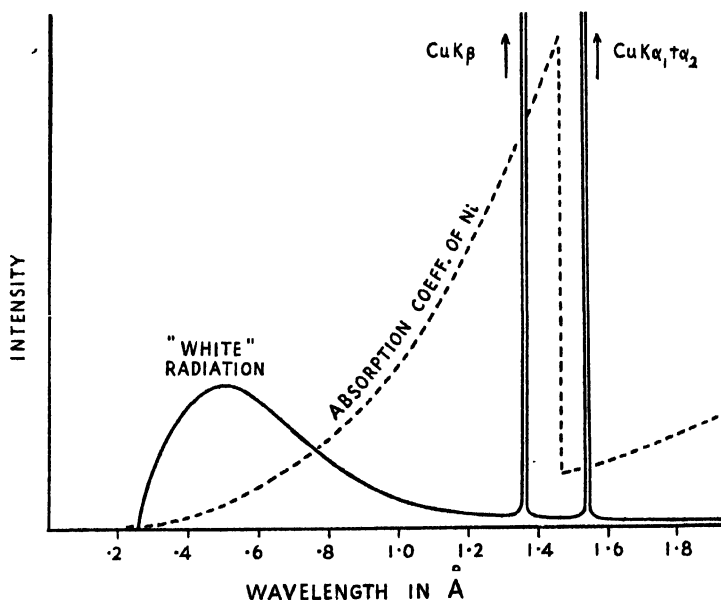


FIG. 70. X-Ray Emission Intensity from a Copper Target at 50,000 Volts and the Absorption Coefficient of Nickel.
(After C. W. Bunn, *Chemical Crystallography*.)

RADIATION FROM TARGETS

The wavelength of x-rays generated depends inversely on the potential *V*, the value of which, therefore, determines the quality of the rays.

Two main features are exhibited by x-rays from the target; a 'white', or background, radiation containing a continuous range

of wavelengths down to a well-defined minimum value and, superimposed on it, a group of intense monochromatic components at wavelengths characteristic of the elements in the target material (Fig. 70). The latter constitute the characteristic x-ray emission spectrum of the target element used, each element giving a similar spectrum but displaced towards shorter wavelengths with increasing atomic number (page 491). Fig. 70 shows the two components of shortest wavelength emitted by Cu, the K_β and the K_α doublet, at 1.39 and 1.54Å respectively.

Characteristic radiations are largely used as a source of monochromatic x-rays, choice of wavelength being effected by using different target elements (Table 25). Demountable tubes permitting exchange of targets are seen to be advantageous where the range of investigations undertaken calls for different wavelengths. Metal targets ranging from chromium to gold are used, since metals have high melting points and good thermal conductivities.

TABLE 25
RADIATION FROM DIFFERENT TARGET ELEMENTS

Anticathode (target)	Wavelengths in Angstroms		Filters for $\frac{IK_\beta}{IK_\alpha} = \frac{1}{600}$		Transmission factor for the K_α line	
	K_{α_2} K_{α_1}	K_β	Material	Thickness		
				g./cm. ²		mm.
Silver	0.564 0.559	0.497	Rhodium ($\lambda_K = 0.534$)	0.096	0.079	0.29
Molybdenum	0.714 0.709	0.632	Zirconium ($\lambda_K = 0.688$)	0.069	0.108	0.31
Copper	1.544 1.540	1.392	Nickel ($\lambda_K = 1.487$)	0.019	0.021	0.40
Cobalt	1.793 1.789	1.621	Iron ($\lambda_K = 1.743$)	0.014	0.018	0.44
Iron	1.940 1.936	1.757	Manganese ($\lambda_K = 1.895$)	0.012	0.016	0.46
Chromium	2.294 2.290	2.085	Vanadium ($\lambda_K = 2.268$)	0.009	0.016	0.50

¹ A. Guinier, *X-ray Crystallographic Technology*, (Hilger and Watts, London) 1952.

INTERACTION OF X-RAYS WITH MATTER

The intensity I with which a beam of initial intensity I_0 emerges after passage through an absorbing sheet of thickness d is given by

$$I = I_0 e^{-\mu d} \quad . . . (1)$$

where μ is the linear absorption coefficient. In practice, the mass absorption coefficient μ_m defined as $\mu_m = \mu/\rho$, where ρ is the density, is more convenient as it is independent of the physical state of aggregation of the absorbing material and depends only upon the elements present in the absorber and the wavelength of the radiation.

MONOCHROMATIZATION BY FILTERS

Fig. 70 shows also the variation of μ_m with wavelength for Ni. The wavelength 1.49\AA at which the sudden and large rise of absorption occurs, lies between the wavelengths of the K_α and K_β radiations from Cu. When Cu radiation is passed through thin Ni foil, the K_β rays at 1.39\AA are heavily absorbed while the K_α doublet is much less affected. By choosing a suitable thickness of Ni (Table 25), the K_β may be reduced to $1/600$ of the intensity of the K_α rays, thus forming a sensibly monochromatic beam, since the white radiation is relatively weak.

The method is of general application. Filters whose absorption edge lies between the K_α and K_β wavelengths for some of the common target elements are included in Table 25.

FLUORESCENCE

Many compounds, *e.g.* willemite, barium platino-cyanide, cadmium tungstate and zinc sulphide, fluoresce under the influence of x-rays. These materials, coated on screens, have been used in the past as detectors of intense x-ray beams, but are now replaced by more efficient phosphors¹, *e.g.* activated zinc cadmium sulphide. Although weak reflections from crystals are not generally visible, a small screen is valuable for aligning apparatus in the direct beam.

PHOTOGRAPHIC EFFECT

Exposure of a photographic emulsion to an x-ray beam and subsequent development, produces a blackening proportional to x-ray intensity and time of exposure, within a wide range of densities. Thus a film may be used to obtain a permanent record of directions and relative intensities of the many weak beams in diffraction

¹ H. A. Klasens and W. de Groot, *Phillips Technical Review*, 9, 1947, p. 321.

experiments. Exposure times ranging from ten minutes to many hours are needed, depending on the nature of the specimen and the technique employed.

IONIZATION OF GASES

Atoms or molecules in a gas are split into pairs of oppositely charged ions by x-rays. An electric field, applied by maintaining a potential difference between two metal electrodes placed in the gas, will sweep the ions to the electrodes, the resulting movement of charge constituting an electric current which may be measured on a sensitive instrument. A small container, with a thin window to admit the x-rays, and enclosing the gas and electrodes, is called an ionization chamber; under suitable conditions, the absolute intensity of the x-ray beam may be measured¹. W. A. Wooster and A. J. P. Martin² have described the construction of an argon-filled chamber with associated apparatus to measure and record a large number of crystal reflections.

X-RAY COUNTER DETECTORS

The Geiger counter (described in Chapter XV, p. 528) is a very sensitive detector of weak x-ray beams and may be used with suitable apparatus to give an immediate indication of beam intensity. A full account of developments in the use of Geiger counter x-ray diffractometers is to be found in H. P. Klug and L. E. Alexander³, and of the introduction of proportional and scintillation counters in H. S. Peiser, H. P. Rooksby and A. J. C. Wilson⁴.

DIFFRACTION OF X-RAYS BY CRYSTALS

Although, as with ordinary light, x-rays can have a corpuscular interpretation, they may be regarded as electromagnetic radiation of the same nature as light rays, but with wavelengths several thousand times shorter than visible light. This is of the same order as the interatomic distances in crystals, and it was suggested by M. von Laue that x-rays might be diffracted by crystals just as light waves are by a diffraction grating. In 1912, W. Friedrich and P. Knipping⁵, using a crystal of zinc blende, confirmed this hypothesis and obtained the first diffraction pattern on a photographic plate.

¹ A. H. Compton and S. K. Allison, *X-rays in Theory and Experiment*, (Macmillan, London), 1935.

² *Proc. Roy. Soc.*, A155, 1936, p. 150.

³ *X-ray Diffraction Procedures*, (Wiley, New York), 1954, ch. 5.

⁴ *X-Ray Diffraction by Polycrystalline Materials*, (Inst. Physics, London), 1955.

⁵ W. Friedrich, P. Knipping and M. Laue, *Le Radium*, 10, 1913, p. 47.

Each atom in a crystal scatters x-rays in all directions. When a narrow pencil of rays is incident upon such a regular array, if a direction exists such that the scattered waves from each of the three axial rows of atoms are simultaneously in phase, then a diffracted beam will arise in that direction.

W. L. Bragg showed that all the observed diffractions could be considered as a special form of 'specular' reflection of the x-rays from the atomic net planes.

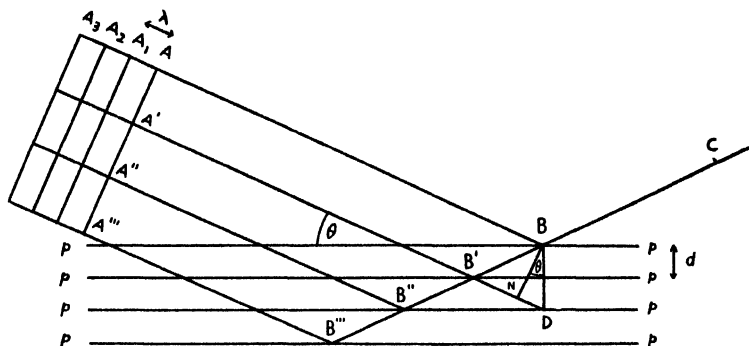


FIG. 71. The Reflection of X-Rays from Atomic Planes.
(After W. L. Bragg, *The Crystalline State*.)

Consider a beam of x-rays of wavelength λ incident at a glancing angle θ upon a set of planes of spacing d_{hkl} (Fig. 71). The condition for reinforcement in the reflection direction C requires that each adjacent component A , A' , A'' , initially in phase, shall remain in phase after reflection. This will obtain if the difference in the paths traversed by adjacent rays is an integral multiple n of the wavelength λ . Commencing in phase, rays A and A' follow paths ABC and $A'B'BC$, and since $BB'D$ is an isosceles triangle, $B'B = B'D$. Thus the path difference $A'B'B - AB = B'B - B'N = B'D - B'N = ND = 2d \sin \theta$.

Bragg's law is therefore:

$$n\lambda = 2d \sin \theta \quad \dots (2)$$

Bragg reflection of x-rays occurs over a few seconds of arc at, and only at, a set of glancing angles $\theta_1, \theta_2, \theta_3 \dots$ which satisfy equation (2) for values of $n = 1, 2, 3, \dots$ called the order of reflection. Since $\sin \theta$ may not exceed one, the number of orders is limited and only those planes for which d is greater than $\lambda/2$ reflect. Atomic plane spacings may therefore be calculated if the Bragg angles are measured using x-rays of known wavelength.

THE BRAGG X-RAY SPECTROMETER

The form of apparatus (Fig. 72) employed by W. H. Bragg and W. L. Bragg for crystal analysis consists of an x-ray tube, a rotating arm on which the crystal is mounted and a tube or ionization chamber filled with sulphur dioxide gas. A pencil of x-rays, obtained by passing the beam through two narrow slits in pieces of lead sheet, is diffracted from the crystal into the ionization chamber. The latter is pivoted on the same vertical axis as the rotating arm carrying the crystal and can be moved over a graduated circle. It contains an electrode which is connected to an electroscop. The crystal

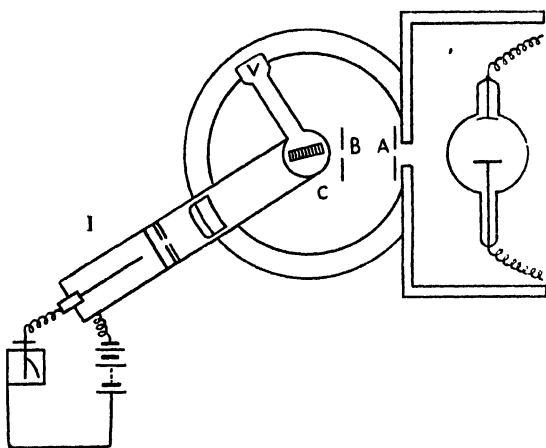


FIG. 72. X-Ray Spectrometer.

A, B. Lead slits.

C. Crystal.

I. Ionization Chamber.

V. Rotating arm moving over graduated circle.

(After J. R. Partington, *Text-book of Inorganic Chemistry*,
(Macmillan, London).)

is set so that the glancing angle θ satisfies Bragg's relation and the diffracted beam is then detected by its action on the ionization chamber and consequent discharge of an electroscop. The angle through which the beam is deflected is 2θ . To record higher orders the crystal is reset to give the appropriate glancing angle and the chamber rotated through twice this angle. Indeed, in more recent versions of this instrument, mechanical gears are used to ensure that angular movement of the detector is always twice that of the crystal table. The Geiger counter replaces the ionization chamber when speed of operation is desirable.

CRYSTAL MONOCHROMATOR

Suppression of the K_{β} emission spectrum by a selective filter leaves a beam containing a strong K_{α} line and the background radiation. The latter may fog films and render observation of low intensity diffraction effects difficult. Crystals provide a more effective way of monochromatization, but at the expense of beam intensity.

The raw beam from the target is collimated and allowed to fall upon a crystal face set at the correct angle for Bragg reflection of the K_{α} wavelength λ_0 . In such a position the only wavelengths reflected will be λ_0 and its 'harmonics' $\lambda_0/2$, $\lambda_0/3$ etc.; the latter are generally feeble. The reflected K_{α} rays may then be used as a monochromatic source.

Stable crystals giving strong reflections are of course preferred. H. Lipson, J. B. Nelson and D. P. Riley¹ described investigations of many suitable materials, including NaCl, LiF and penta-erythritol, the latter giving a particularly strong (002) reflection.

X-RAY DIFFRACTION TECHNIQUES AND THEIR INTERPRETATION

A crystal structure is completely specified by the dimensions and shape of the unit cell and the positions of the atoms within it. The unit cell geometry governs the orientation and spacing of net planes, and hence directions of diffraction, while the nature and disposition of the atoms within the cell determine the population of these planes and hence the diffraction intensities.

THE DEBYE-SCHERRER POWDER METHOD

The Bragg reflections from a number of (*hkl*) planes are simultaneously recorded on a film using a monochromatic beam, the known wavelength of which enables the interplanar spacings to be calculated from the diffraction angles.

The material to be investigated is prepared in the form of a very thin cylinder of finely divided powder consisting of a large number of randomly orientated crystallites, the specimen being placed perpendicular to, and in the path of, the collimated beam of x-rays (Fig. 73).

Consider reflections from, say, the (111) planes. Among the numerous crystals there will be a number in which the (111) planes are orientated with respect to the beam at the Bragg angle θ required to give a reflection. Regardless of orientation round the beam axis, each will give a diffracted beam deviated by 2θ . Thus all the (111) reflections will lie along the surface of a cone of semi-angle 2θ

¹ *J. Sci. Instr.*, **22**, 1945, p. 184.

with the beam as axis. If the crystallites are sufficiently numerous and the specimen continuously rotated, these individual reflections coalesce to give a separate continuous conical surface for each set of (hkl) planes.

In the powder camera these cones intersect a cylindrical strip of film concentric with the specimen, in pairs of arcs from which the Bragg angle needed to find the interplanar spacings may be calculated.

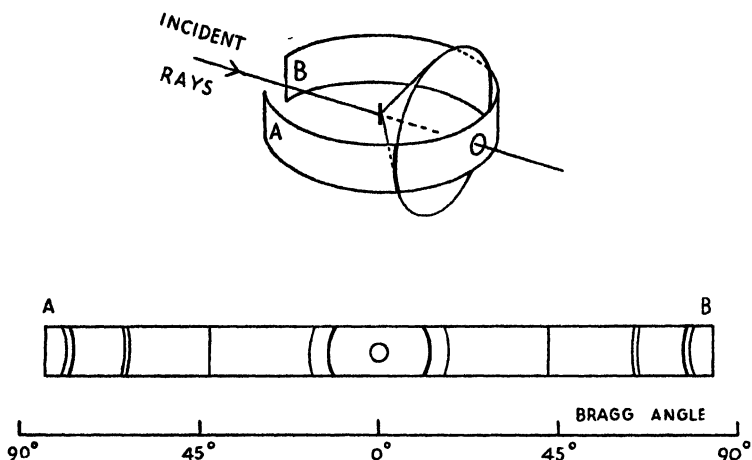


FIG. 73. Formation of a Debye-Scherrer Powder Photograph on a Cylindrical Film.

(A. Taylor, *An Introduction to X-Ray Metallography*.)

THE 19 CM. POWDER CAMERA

The construction of a standard camera is shown in Fig. 74 which depicts the main features of all such instruments. The x-ray beam, after filtering by a suitable foil (F), is collimated into a beam of rectangular cross-section (about 4 mm. by 1 mm.) which then falls upon the specimen (S). The undeflected beam passes into a beam trap (T) to reduce unwanted fogging of the film by scattering. To record diffraction arcs the film, in two separate strips, is placed in cassettes, one on each side of the beam, round the periphery of a 19 cm. diameter cylinder. On each side of the exit aperture of the camera a metal knife-edge (K) is placed immediately in front of the film. This intercepts the scattered background and terminates the exposed part of the film by a sharp edge. As the knife-edge separation is known, the circumferential distance between

the pairs of arcs may be determined, the Bragg angle calculated and the interplanar spacings deduced from equation (2).

For crystals giving relatively few widely spaced lines, a 6 cm. diameter camera may be used with advantage, since the shorter working distance decreases the exposure times required. For complex diagrams or work of high accuracy, 19 cm. and even 35 cm. diameter cameras are used.

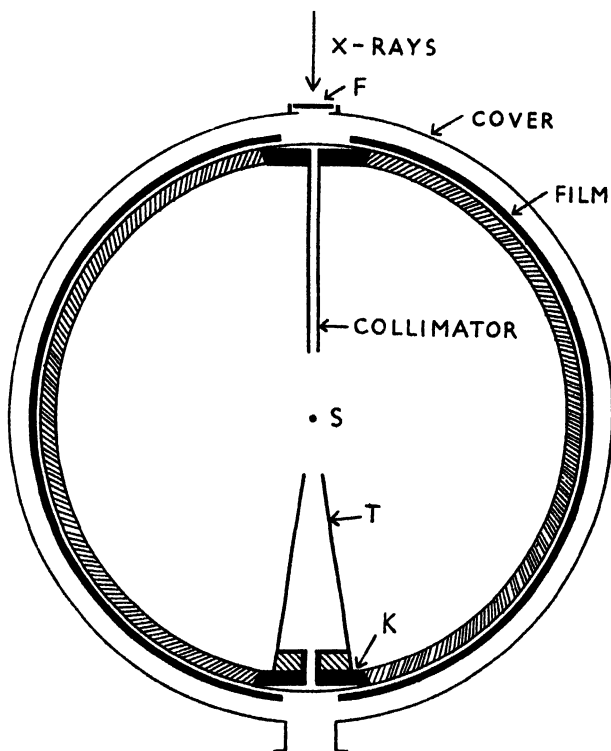


FIG. 74. Essential Features of an X-Ray Powder Camera.

SMALL ANGLE DIFFRACTION

The knife edges in standard cameras prevent the recording of low angle powder lines from planes of spacing greater than about 13\AA in the most favourable case, *i.e.*, using CrK_α radiation. This limitation is a serious disadvantage in clay and soil analysis. The important basal spacings in montmorillonite (14\AA), chlorite (14\AA),

nacrite (43Å) and many others, could not be recorded on these otherwise excellent cameras. D. M. C. MacEwan¹ has described a suitable 9 cm. camera for clay minerals. The beam trap and knife edges are dispensed with, the unabsorbed x-ray beam passing through a 5 mm. wide rectangular aperture in the film. Plane spacings up to 55Å and 75Å may be recorded using CuK_α and CrK_α radiation respectively. At such small angles the general scattering by air is serious and it is necessary to evacuate the camera and to use a strictly collimated monochromatic beam of x-rays produced by crystal reflection.

FILM MEASUREMENT

Unless extreme accuracy is required, the circumferential distance may be measured conveniently by holding the films on a flat sheet of opal glass (illuminated from below) by means of a steel ruler with the measuring edge along the arc centres. A hand-lamp and reading lens enable the distance of the arcs from the knife-edge shadows to be read directly. Precise powder diagram analysis requires a vernier measuring rule. Correction must then be made for geometrical errors in the powder camera, the shape and absorption of the specimen and film shrinkage, details of which will be found in A. Guinier².

ACCURACY OF PLANE SPACING MEASUREMENTS

A small error in measuring the position of a line in the forward direction results in a relatively large error in d .

The error Δd in d arising from a given small error $\Delta\theta$ in the measurement of θ may be calculated from Bragg's law (equation (2) p. 471). By differentiation:

$$0 = 2\Delta d \sin \theta + 2d \cos \theta \Delta\theta$$

$$\text{Thus: } \frac{\Delta d}{d} = - \frac{\Delta\theta}{\tan\theta} \quad \dots (3)$$

For Bragg angles approaching 90° (*i.e.*, in the back reflection region), the *relative* error in d becomes small, since $\tan \theta$ becomes very large. High angle powder lines are much used in precision determination of lattice constants.

POWDER SPECIMENS

The specimen is ground in a mortar and the larger particles removed

¹ *J. Soil Sci.*, 1, 1949, p. 90.

² *loc. cit.*

by passing through a fine sieve¹. Too much grinding may lead to deformation of the structure of the crystallites, but such distortion may be reduced by careful crushing² and annealing.

Several methods are in use for forming the powder into a straight cylinder a few tenths of a millimetre in diameter. In one³, a Lindemann glass fibre is thinly coated with a very small quantity of gum (canada balsam, gum tragacanth, etc.), and then rolled in the powder by hand or with the aid of a glass slide until a uniform coating is obtained. The glass and gum contain amorphous arrangements of light atoms from which scattering is feeble. Alternatively, the powder may be packed into thin-walled Lindemann glass or cellophane tubes⁴, or made self-supporting by mixing the powder with a gum and extruding through a cylindrical die⁵.

The specimen or its supporting fibre is fixed to the specimen holder by a small piece of wax, inserted in the camera, and aligned accurately on the camera axis by means of the mechanical adjustments provided.

INTERPRETATION OF POWDER DIAGRAMS

Analysis of the powder diagram yields a set of interplanar spacings d_{hkl} but no information concerning the orientation of those planes in the crystal. The latter is a serious limitation and restricts powder methods to analysis of simple structures, or to identification of minerals by comparison with standard powder diagrams.

Interplanar spacings for each of the seven Bravais unit cells may be expressed in the form of equations containing the angles and dimensions of the unit cell. If, therefore, the spacings calculated from the powder diagram can be fitted to such a formula by correct choice of these constants, the lattice is determined. This process is feasible only if the number of constants is small.

CUBIC CRYSTALS

The interplanar spacings d_{hkl} are related very simply for crystals of the simple cubic class. $d_{100} = a$, $d_{110} = a/\sqrt{2}$, $d_{111} = a/\sqrt{3}$, $d_{210} = a/\sqrt{5}$ etc., where a is the side of the unit cell. Such a sequence may be recognised by inspection; identification of d_{100} gives directly the unit cell dimension a .

¹ A. Taylor, *An Introduction to X-ray Metallography*, (Chapman and Hall London), 1945.

² O. von Knorring, G. W. Brindley and K. Hunter, *Miner. Mag.*, **29**, 1957, p. 963.

³ M. J. Buerger, *Amer. Min.*, **21**, 1936, p. 11.

⁴ K. Lonsdale and H. Smith, *J. Sci. Instr.*, **18**, 1941, p. 133.

⁵ J. S. Lukesh, *Rev. Sci. Instr.*, **11**, 1940, p. 200.

CRYSTALS OF LOWER SYMMETRY

A graphical method introduced by A. W. Hull and W. P. Davey¹ is used to determine the two lattice constants a and c for tetragonal and hexagonal crystals. A set of curves depicting the relative values of d_{hkl} for a range of values of a/c is prepared, and the value of the latter, for which observed spacings match the graphical ones, determined by inspection. The lines may then be indexed and the size of the unit cell calculated. Details of graphical methods are given by N. F. M. Henry, H. Lipson and W. A. Wooster² and C. W. Bunn³. A set of Bunn charts for these purposes has been made available by the *Institute of Physics*.

Graphical methods are limited generally to cubic, tetragonal and hexagonal crystals; the more powerful single crystal methods are essential for the remaining classes.

SINGLE CRYSTAL METHODS

Each of the crystallographic axes in a crystal is characterized by the fact that in this direction identical atoms, groups of atoms or

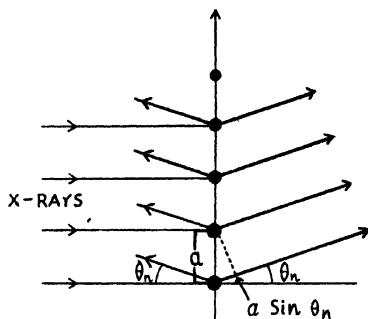


FIG. 75. Scattering of X-Rays by a Line of Equally Spaced Atoms.

molecules are spaced at regular intervals. When a small single crystal is set up with one of these axes perpendicular to a fine monochromatic x-ray beam, reinforcement of wavelets scattered from adjacent atoms occurs in a direction θ_n if:

$$a \sin \theta_n = n\lambda \quad \dots (4)$$

where n is an integer and a the atomic spacing along the axis,

¹ *Phys. Rev.*, 17, 1921, p. 549.

² *The Interpretation of X-ray Diffraction Photographs*, (Macmillan, London), 1951.

³ *Chemical Crystallography*, (Clarendon Press, Oxford), 1945.

conditions to be realized from time to time, and as the crystal passes through these settings a momentary diffracted beam flashes out along the surface of one of the cones.

A cylindrical film placed coaxially about the axis of rotation will intercept the cones in a set of horizontal circles (Fig. 76) along which will lie the discrete diffraction spots. When the film is unrolled, a set of straight 'layer lines' of spots can be seen (Pl. 20;) when a crystal is rotated about the x axis, for instance, planes $(0, k, l)$ parallel to the axis produce the zero layer line passing through the central exit aperture, while those with indices $(1, k, l)$ give the adjacent first order layer line ($n = 1$), and so on.

UNIT CELL DIMENSIONS

The atomic spacing a may be calculated very simply from the layer line separations on the film. If y is the perpendicular distance between the zero and first order layer lines, then

$$\tan \theta_1 = y/R \quad \dots (5)$$

where R is the radius of the film when in position on the camera. θ_1 may then be substituted in equation (4) and a calculated for $n = 1$. Higher order layers corresponding to $n = 2, 3 \dots$ may be used similarly to obtain several values for a and a mean value derived. In view of the small number of layer lines usually apparent and the finite size of the spots, an accuracy not better than one part in a hundred may be expected from this measurement.

If the crystal can be set to rotate about each of the three crystallographic axes in turn, the lengths and directions of the unit cell edges may be determined. A study of the crystal habits by optical methods will usually suggest axes to try; the extent and nature of the information to be derived from these methods are considered by N. H. Hartshorne and A. Stuart¹ and C. W. Bunn².

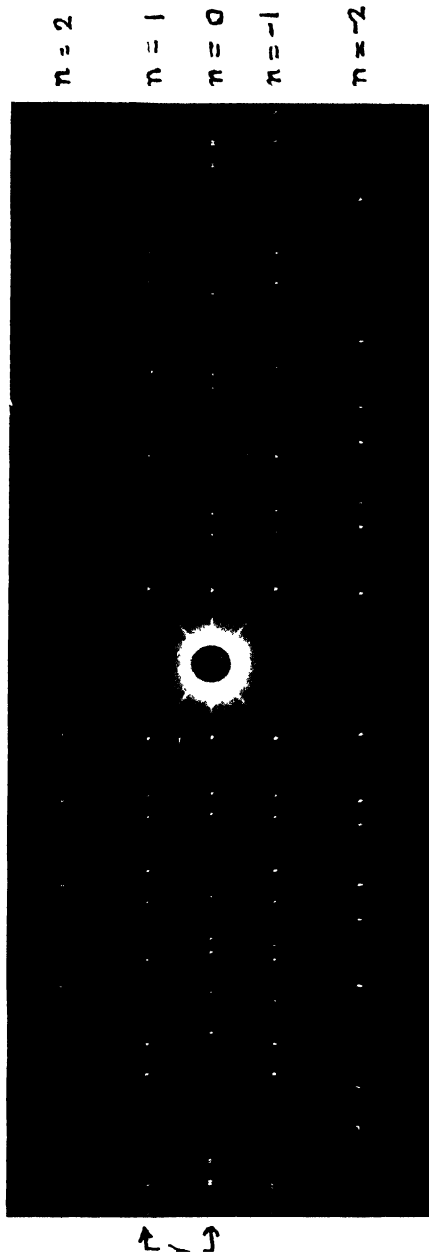
SINGLE CRYSTAL SPECIMENS AND APPARATUS

Absorption effects require that single crystals should be small so that diffracted beams are not attenuated during passage through the crystal. Crystals free from flaws and twinning, having linear dimensions of a few tenths of a millimetre, with roughly equal development along each axis, are generally suitable.

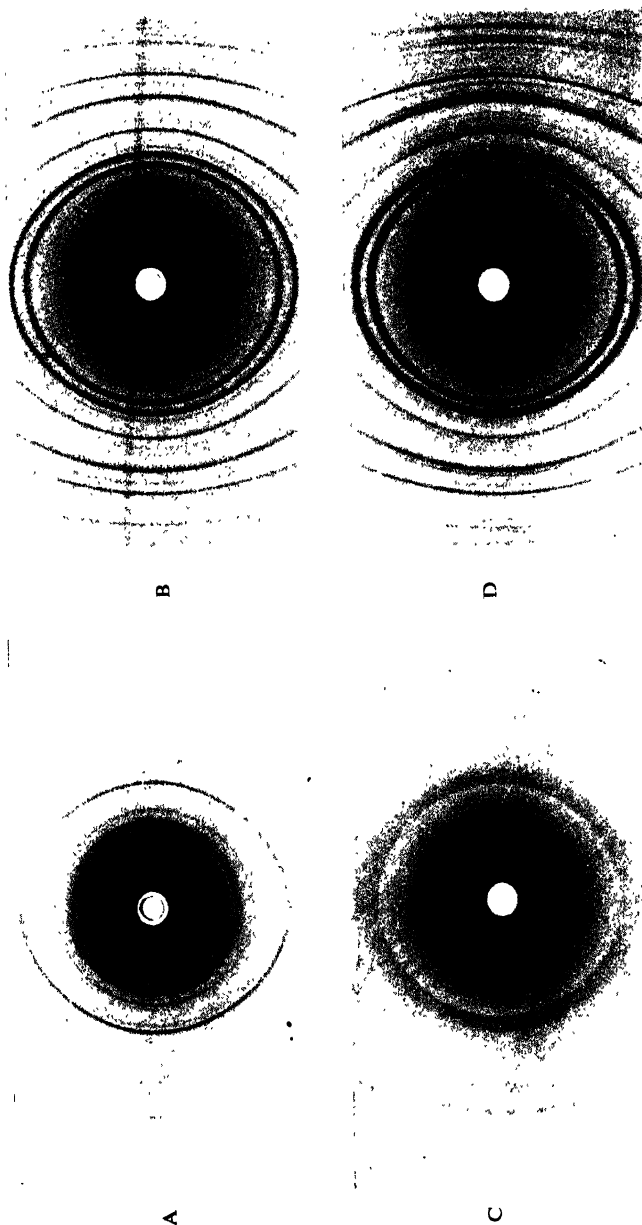
The *Unicam* single crystal camera carries a goniometer head on which the crystal, attached to a Lindemann glass fibre by gum, may be mounted. The goniometer, mounted on a motor driven

¹ *Crystals and the Polarizing Microscope*, (Arnold, London), 1934.

² *Op. cit.*



SINGLE CRYSTAL C-AXIS ROTATION PHOTOGRAPH OF 2-QUARTZ SHOWING ZERO, FIRST AND SECOND ORDER LAYER LINES.
(Courtesy: Vaca Laboratories, General Electric Company, Stamming, Middlesex)



X-RAY POWDER DIAGRAMS OF (A) NACRIT, (B) DICKIT, (C) HALLOYSIT AND (D) KAOLINIT.
 (Courtesy G. F. Claringbull, Dept. of Mineralogy, British Museum (Natural History), London).

spindle, has arcs and traverses to orientate and align the crystal on the rotation axis of the camera. Initial settings are made optically, the final adjustment by interpretation of the resulting diffraction pattern.

Several kinds of film cassette, cylindrical and flat, may be attached to the instrument. The 6 cm. diameter cylindrical cassette fits over the crystal mounting and is coaxial with the axis of rotation. The film is located on the inside wall by a small flanged tube passing through a hole punched in the film and through which the unabsorbed beam leaves the system. A larger hole in the cassette wall opposite admits the collimator.

ATOMIC CONFIGURATIONS

The positions of atoms in the unit cell determine the constitution of each set of net planes and hence affect the intensity of Bragg reflections from them. Once the unit cell has been determined, the diffraction intensities provide a means of finding the detailed atomic arrangement.

The relative intensities of the diffracted beams are generally found indirectly from the optical densities of the spots they produce on the film. For many purposes, visual comparison with a set of graded exposures is sufficient and, indeed, comparable in accuracy with the more complicated photometric methods used to find the total effective blackening in a spot (K. Lonsdale)¹.

No general method exists by which the atomic positions within the unit cell may be inferred directly from the recorded intensities. The two approaches to the problem both contain an element of intuition based on experience. In the 'trial and error' method, a trial atomic structure is taken and the diffraction intensities it would give rise to compared with the observed values and the model adjusted until agreement is reached. The *Fourier Synthesis* method utilizes the fact that the several orders of reflection from a given set of net planes represent the squares of amplitudes of successive terms in the Fourier series describing periodic variation of electron density perpendicular to those planes. The relative phase of these contributions is not, however, generally known and cannot be obtained experimentally. With a suitable choice of phases, electron density maps are built up, atoms appearing as large local concentrations. Details of these methods are beyond the scope of this chapter; for an elementary account the reader is referred to J. M. Bijvoet, N. H. Kolkmeier and C. H. MacGillavry².

¹ *Crystals and X-rays*, (G. Bell, London), 1948.

² *X-ray Analysis of Crystals*, (Butterworths Scientific Publications, London), 1951.

THE LAUE PHOTOGRAPH

When a stationary single crystal is irradiated with 'white' radiation containing a continuous range of wavelengths, each set of (*hkl*) planes reflects the wavelength for which, at that angle of incidence, Bragg's Law holds. Thus a large number of net planes act simultaneously as simple mirrors and the resulting diffraction pattern records their relative orientation. The fact that the planes select different wavelengths to reflect, prevents use of the method for structure analysis.

ORIENTATION OF CRYSTALS

Laue diagrams provide essentially the same information obtainable by optical goniometer studies, but with power to do so, even when the specimen shows little or no development of faces. An important use of the Laue method is concerned with the symmetry properties of the atomic lattice. The planes of indices (*0, k, l*) are parallel to the *x* axis and in a cubic crystal, for example, are such that rotation of the crystal through 90° brings the lattice back to its original appearance. This zone axis is said to be fourfold. The mirror-like action in the Laue method produces a set of spots having this fourfold symmetry when the X-ray beam is incident along this axis. The directions and symmetries of zone axes found in this way can be a great assistance in structure determinations.

An example of interest to gemmologists may be found in a paper by B. W. Anderson¹ describing the application of Laue's method to the discrimination of natural and culture pearls, the obvious advantage of the method being that the destruction of a valuable gem stone is avoided². Applying Laue's method of diffraction patterns, natural pearls are found to give a hexagonal spot pattern in all positions, whereas culture pearls give a rectangular or unsymmetrical pattern unless the nacre layers of the nucleus happen to be normal to the X-ray beam. The difference arises from the radial arrangement of the trigonal axes of the minute CaCO₃ crystals in natural pearls and the parallel arrangement of these crystals in the mother of pearl nucleus. A pencil of X-rays incident along any diameter of a natural pearl will give a six-fold pattern, while only one such axis exists in a culture pearl.

X-RAYS AND MINERAL STRUCTURE

The power of X-ray methods to reveal detailed atomic arrangement in minerals has led to the introduction of classifications which show

¹ *Brit. Journ. Radiology*, **49**, 1932, p. 57.

² See Chapter XII, p. 459.

mineral relationships more clearly than is possible by studying their complex chemical formulae. 'Minerals are very seldom simple chemical compounds. Isomorphous substitution is the rule rather than the exception. . .¹'; this statement serves to illustrate the complex structural chemistry of minerals. The concept of isolated molecules having the chemical proportion of the whole crystal is found to be untenable in many cases. Certain atoms (O, Al) are found to have two different roles in the structure depending on their location. Oxygen, for instance, occurs in some minerals in both strong Si-O networks and hydroxyl ions (OH). Chemical determination of oxygen in such cases may not show this duality. At the same time, atomic arrangements furnish explanations of many of the important physical properties by which, earlier, mineralogists classified minerals, thereby confirming the essential correctness of this procedure. Many examples will be found later in the chapter, of the classification of minerals into related groups, based on their general structural similarity.

ATOMIC STRUCTURE OF MINERALS

Among the first minerals to yield to x-ray analysis in the hands of W. L. Bragg² were NaCl, CaF₂, ZnS, FeS₂, and CaCO₃. In each case, morphology is good, crystal class and axes known. Thus Bragg was able to use the ionization spectrometer to record intensities of reflections from a large number of known (*h*, *k*, *l*) planes. The unit cell dimensions were fixed by using Bragg's law and the intricate problem of the atomic positions within the cell solved by detailed consideration of reflection intensities.

Knowledge of the atomic structure of calcite and aragonite leads to a better understanding of their physical properties. The CO₃ radical occurs in each as a planar group, with the small carbon atom at the centre of an equilateral triangle of oxygen atoms. It is to this group, chiefly, that the large birefringence of both forms is due. Oxygen atoms are readily polarized by the electric field of a light wave, but owing to planar arrangement, the effect is markedly different, depending on whether the electric field is perpendicular to, or in, this plane. Calculation of relative refractive indices for these different directions, based on this concept, was first published by W. L. Bragg³. By contrast, sulphates, in which the radical is an isotropic arrangement of the four oxygens round the sulphur, are only weakly birefringent.

¹ W. L. Bragg, *Atomic Structure of Minerals*, (Cornell University Press), 1937.

² *Proc. Roy. Soc.*, A89, 1914, p. 468.

³ *Proc. Roy. Soc.*, A105, 1924, p. 370.

Silicates. The general classification set forth by W. L. Bragg¹ depends upon behaviour of the SiO_4 group which forms a tightly bound regular tetrahedron of the four oxygen atoms enclosing the small Si atom. Olivine ($9\text{Mg}_2\text{SiO}_4\text{Fe}_2\text{SiO}_4$) contains independent SiO_4 radicals held together in layer formation by metallic ions². This structure is characteristic of many minerals including forsterite, fayalite and monticellite. Mg, Fe and Ca, which make up the rest of the structure, replace each other in the various forms. The related chondrodite minerals have layers of the olivine structure alternating with MgOH layers parallel to the (001) plane. Determination of the (001) plane spacing thus permits positive identification in terms of an integral number of layers, each of known thickness. The more complex garnets still retain independent SiO_4 tetrahedra which pack together in such a way as to surround each aluminium atom with eight oxygen atoms in an octahedral formation.

Co-ordination. The occurrence of tetrahedral and octahedral co-ordination groups of oxygen atoms round the smaller Si and Al atoms led L. Pauling³ to propose a set of co-ordination rules which form the basis of the stereochemistry of minerals. These rules are based on the relative size of the ions and the necessity to satisfy the valence charge of each ion by proper choice of the charge and co-ordination of its nearest neighbours. Indeed, the non-existence of Fe and Mg aluminosilicates can be deduced from the difficulty of satisfying these conditions.

Amphiboles and Pyroxenes. The fibrous nature of asbestos and its main constituent chrysotile, and characteristic cleavages in other minerals of this group, are readily explicable in terms of crystal structure. In the pyroxene group, the SiO_4 tetrahedra are linked in indefinitely long chains by making one of the oxygen atoms common to adjacent tetrahedra. In diopside⁴ ($\text{CaMg}(\text{SiO}_3)_2$), these chains lie parallel to the *c* axis of the monoclinic unit cell, held together laterally by the Ca and Mg ions. Amphiboles are similar, but possess double chains formed by further sharing of the tetrahedral oxygen atoms. The relatively weak lateral binding gives rise to the easy cleavage parallel to the chains.

An important contribution of x-ray methods to clarification of the chemistry of these compounds arises from the recognition that some of the oxygen atoms present in the amphibole tremolite, for example, are not involved in the SiO_4 groups, but occur in separate

¹ *Op. cit.* (1937).

² W. L. Bragg and G. B. Brown, *Z. Krist.*, **63**, 1926, p. 538.

³ *J. Amer. Chem. Soc.*, **51**, 1929, p. 1010.

⁴ B. Warren and W. L. Bragg, *Z. Krist.*, **69**, 1928, p. 168.

hydroxyl groups. The ideal chemical formula for this mineral is thus written $(\text{OH})_2\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}$ to make this distinction.

It will be observed that the concept of acid radicals, or a molecular type of structure, disappears in these extended configurations and the chemical formulae obtained from analysis no longer give an adequate guide to the ionic groupings.

Mica and Clay Mineral Layer Lattices. In all these minerals the SiO_4 tetrahedra are linked together by common oxygen atoms to form extended plane sheets, three oxygen atoms from each group lying in this plane linked to form a hexagonal network, above which the remaining oxygen atoms at the vertices of the SiO_4 tetrahedra form a second parallel layer.

The mica type of structure consists of pairs of these layers with the oxygen vertices pointing inwards, firmly bound together with metallic ions (Al in muscovite, Mg and Fe in biotite) and including hydroxyl groups between the vertices (Fig. 77). These composite layers are then cemented together rather weakly by potassium ions in muscovite and sodium ions in paragonite. The chemical formula $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ for muscovite therefore represents alternate layers of composition 2K and $2(\text{Al}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2)$ which together are about 10\AA thick.

These structural formulae are idealized. Although the oxygen content remains constant over a range of related minerals, extensive mutual replacement of Si by Al and Al by Mg or Mg and Fe, gives rise to a great range of chemical compositions based on the same general structure.

L. Pauling¹ proposed a similar layer structure for talc, in which all the Al is replaced by Si giving the double sheets the composition $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$. Such sheets are electrically neutral, which accounts for lack of further ions binding them together to form the repeated layer structure.

The relatively weak binding between the successive main layers explains the prominent cleavage habits of micas. In margarite, where these layers are cemented by doubly charged Ca ions, cleavage is more difficult than in muscovite, while in talc the absence of these ions leads to extreme softness.

An important mineral group having the mica layer structure is chlorite for which L. Pauling² proposed a structure of alternating mica and brucite layers $(\text{Mg}_2\text{Al}(\text{OH})_6)$ giving a total layer thickness of about 14.3\AA (Fig. 77). Later detailed analyses^{3, 4} have confirmed

¹ *Proc. Nat. Acad. Sci.*, **16**, 1930, p. 123.

² *Proc. Nat. Acad. Sci.*, **16**, 1930, p. 578.

³ R. C. McMurchy, *Z. Krist.*, **88**, 1934, p. 420.

⁴ G. W. Brindley, B. M. Oughton and K. Robinson, *Acta Cryst.*, **3**, 1950, p. 408.

Pauling's ideas generally; the many polymorphic forms having the same general structure may be explained by isomorphous replacement of metallic ions and various stacking sequences of the layers.

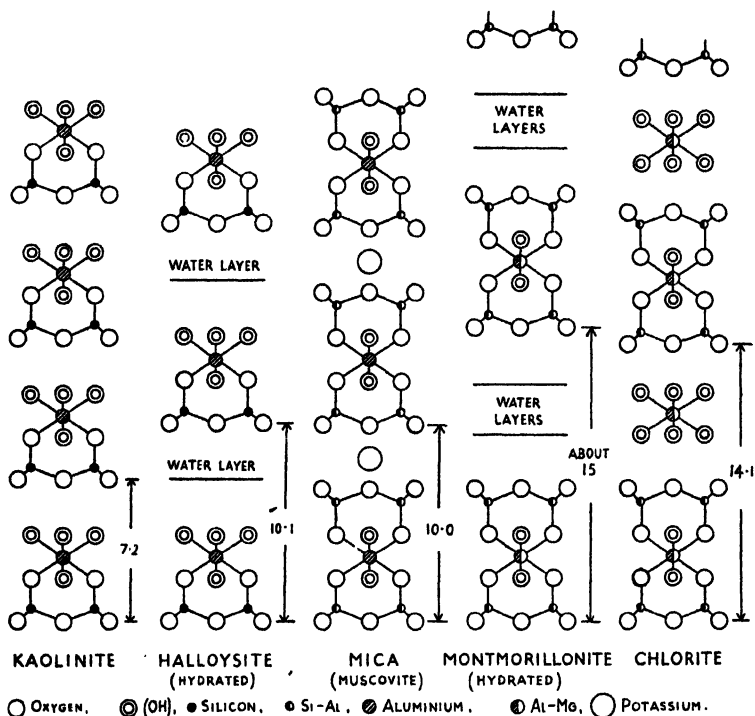


FIG. 77. Layer Structures of a Number of Silicates.

Approximate basal spacings in kX units (1 kX unit = 1.002 Å.)

(After G. W. Brindley, *X-Ray Identification and Crystal Structures of Clay Minerals*.)

*Clay Minerals*¹. x-rays are now widely used to identify clay constituents, minuteness of the crystallites making other methods difficult. The layer structure in mica is common to all clay minerals which have accordingly a flaky habit. The chief differences are due to existence of single layers and the manner of their alternations. A full account of x-ray methods and results is given by G. W. Brindley².

¹ See also Vol. II, Ch. III.

² *X-ray Identification and Crystal Structures of Clay Minerals*, (Mineralogical Society, London), 1951.

The powder diagram method is used generally, with the modifications, mentioned earlier, required by the large basal plane separations encountered. The detailed atomic positions have been inferred from a knowledge of the constitution of the layers and measurement of layer separations.

Kaolin Minerals. L. Pauling¹ proposed a structure for kaolinite subsequently confirmed in detail by J. W. Gruner². The basic layer consists of the plane network of SiO_4 tetrahedra with a layer of hydroxyl groups above the vertices, forming close packing round Al atoms (Fig. 77), the whole layer, of thickness 7.2\AA , having the sequential formula $\text{O}_3\text{Si}_2\text{O}_2\text{OHAl}_2(\text{OH})_3$. Kaolinite is built from a series of such layers, the tetrahedra all pointing in the same direction, the triclinic unit cell³ containing one layer only.

The polymorphism of the related mineral series nacrite-dickite-halloysite-kaolinite, each of which has the same chemical formula, has been studied by S. B. Hendricks⁴. These minerals represent different ways of stacking the unit layers. In nacrite, for instance, the cell height c perpendicular to the layers is about 43\AA , indicating that six such layers are required before the structure repeats itself. The rather poor basal reflection from halloysite is thought to be due to random mixing of the true nacrite, dickite and kaolinite layers (Pl. 21c).

Montmorillonite—Beidellite. The relative aluminium content of this group is higher than in the kaolinite series, due to the isomorphous replacement of silicon. The resulting change of the balance of electric charges requires incorporation of metallic ions in the layers. Fe, Mg and Ca are commonly found.

Montmorillonite (Fig. 77) consists of pairs of single mica sheets with the vertices of the tetrahedra facing outwards, held together with layers of water molecules giving a total spacing of about 14\AA . The rather indefinite cell height and swelling properties depend on the variability of these water layers and the ease with which water is included or expelled from between the layers. G. Nagelschmidt⁵ suggests a scheme for classifying the system montmorillonite-beidellite-nontronite in the dehydrated form.

Feldspars. The essential structural feature of feldspars, which often appear in quartz-bearing sedimentary rocks of great age, is a three dimensional framework of silicon-oxygen tetrahedra, formed from

¹ *Loc. cit.*

² *Z. Krist.*, **83**, 1932, p. 75.

³ G. W. Brindley and K. Robinson, *Miner. Mag.*, **27**, 1946, p. 242.

⁴ *Z. Krist.*, **100**, 1939, p. 509.

⁵ *Miner. Mag.*, **25**, 1938, p. 140.

four component rings of these groups linked by common oxygen atoms. This basic framework is negatively charged, the requisite positively charged metallic ions lying in the interstices.

This structure was first established by complete analysis of sanidine by W. H. Taylor¹, who made a detailed study of the isomorphous series orthoclase—hyalophane—celsian². The potassium-rich mineral has a monoclinic unit cell and as K^+ is progressively replaced by Ba^{2+} , electrical neutrality is maintained by an equivalent replacement of Si^{4+} by Al^{3+} within the tetrahedra. Celsian is strictly triclinic but departs only slightly from the monoclinic form. The structural changes are thought to be due to distortion of the main framework with varying size of the interstitial metallic ions. Transition from sodium feldspar $NaAlSi_3O_8$ to anorthite $CaAl_2Si_2O_8$ takes place by a progressive replacement of Na^+ by Ca^{2+} and a corresponding replacement of Si^{4+} by Al^{3+} , which accounts for the isomorphism of these two minerals. As in the case of oxygen, the dual role of aluminium as either a constituent of the oxygen tetrahedra or elsewhere with a higher degree of co-ordination, is most important.

Many difficulties remain in classifying feldspars, as may be seen in a recent paper by O. F. Tuttle³, in which four separate series of alkali feldspars are proposed. G. and J. D. H. Donnay⁴, in a study of a series of feldspars, conclude that over the entire range of minerals investigated, solid solution is virtually complete, although a change of symmetry occurs for which the corresponding energy change is too small to detect by differential thermometry.

Zeolites (*e.g.* analcite) have a three dimensional linkage of tetrahedra, but the framework is more open than in the feldspars, thus permitting easy movement of the interstitial ions. Base exchange properties are related to this ionic freedom.

Quartz. Silica (SiO_2) occurs in three crystalline forms, quartz, tridymite and cristobalite, each formed from SiO_4 tetrahedra closely linked to give a very strong three dimensional network and in which every oxygen is a link between two silicon atoms. Each oxygen has therefore a half share in the adjacent silicon which, for the four oxygens in each tetrahedron, gives the ideal formula SiO_2 . In α -quartz, stable below $573^\circ C$, the silicon atoms form a trigonal array, while in β -quartz, stable between $573^\circ C$ and $870^\circ C$, a hexagonal arrangement is found, the difference being in the nature of a distortion with no change in linkage. No direction appears to exist for easy cleavage since Si-O linkages would have to be broken.

¹ *Z. Krist.*, **85**, 1933, p. 425.

² W. H. Taylor, J. A. Darbyshire and H. Strunz, *Z. Krist.*, **87**, 1934, p. 464.

³ *Miner. Mag.*, **29**, 1951, p. 757.

⁴ *Amer. J. Sci.*, Bowen Vol., 1952, p. 115.

The other forms, tridymite and cristobalite, stable in the ranges 870°–1,470°C and above 1,470°C respectively, are due to different linkage schemes of the tetrahedral groups. Their existence in a metastable state at ordinary temperatures is due to the persistence of the particularly strong structures formed, any change to the appropriate stable form taking place with extreme slowness.

MINERAL IDENTIFICATION: X-RAY ABSORPTION

X-ray methods have been developed to provide several non-destructive and rapid methods by which minerals or their constituent elements may be identified. All minerals have not the same opacity to x-rays and this fact has enabled the rays to be successfully applied to the differentiation of precious stones. Some of the results of D. Deolter's¹ work are shown in the following table:

Behaviour to x-rays		
<i>Group 1.</i>	Perfectly transparent.	Amber, diamond.
<i>Group 2.</i>	Strongly transparent.	Corundum and its varieties.
<i>Group 3.</i>	Transparent.	Opal, andalusite, kyanite, chrysoberyl.
<i>Group 4.</i>	Semi-transparent.	Quartz, topaz.
<i>Group 5.</i>	Weakly transparent.	Spinel, grossularite (hessonite).
<i>Group 6.</i>	Translucent.	Tourmaline, apatite, magnetite.
<i>Group 7.</i>	Practically opaque.	Brookite, andradite (melanite), almandine garnet, beryl, epidote, rutile.

This general absorption is governed by the independent scattering power of the atoms of which the mineral is composed and the wavelength of the radiation used, elements of high atomic number causing large absorption. The above method is restricted consequently to a rather broad classification, different minerals of nearly the same chemical constitution having a similar absorption.

W. A. Wooster² has recently shown how variation with wavelength of the scattering power of elements may be used in certain favourable cases to determine the amount of a given constituent in a mineral. Fig. 78 shows the absorption coefficient per g. atom for elements at one particular wavelength. Using Ni K α radiation at 1.66Å, it can be seen that μ_m is very large ($\sim 20,000$) for transition elements Co, Fe and Mn, but much smaller ($\sim 2,000$) for Si, Al, O, Na, etc. Since the total absorbing power of a mineral is the sum

¹ *N. J. Min. Geol. etc.*, 11, 1896, p. 87.

² *Miner. Mag.*, 29, 1950, p. 427.

of the independent effects of its constituents, 5% of iron gives about the same contribution as 50% oxygen.

The small amount of iron present in biotite for example thus contributes substantially to the whole absorption at this wavelength. By calculation, W. A. Wooster shows that the relation between the total absorption coefficient μ_m and the Fe content is linear, which suggests that the variation of μ_m is almost entirely due to changes in the amount of Fe. He concludes that measurement of the absorption of a specimen of biotite would permit an estimation of the Fe to within about 1%.

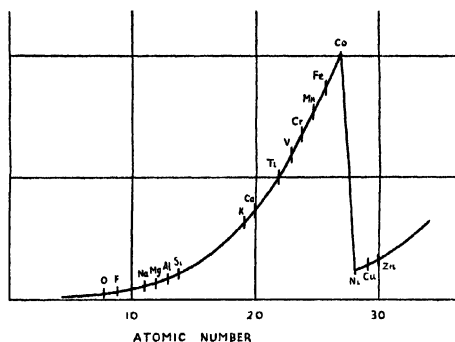


FIG. 78. Variation of Gram-Atomic Absorption Coefficient with Atomic Number.

(After W. A. Wooster, *Min. Mag.*, 29, 1950, p. 427.)

The technique is applicable only in cases where a single element in small concentration has a greatly enhanced scattering power, due to the particular choice of wavelength. For instance, in the example chosen, any Ti present would mask the effect of the Fe. A list of minerals for which the method might be of use includes pyroxenes, amphiboles, garnet, tourmaline and serpentine.

X-RAY SPECTRUM ANALYSIS

The same type of spectrometers are used in x-ray spectrum analysis and in x-ray crystal analysis. When a solid element is bombarded with cathode rays, the K, L, M characteristic radiations are evolved. H. C. Moseley¹, found that the frequency of the strongest line of

¹ *Phil. Mag.*, 6, 26, 1913, p. 1024.

the K series was related to atomic number of the element by the formula:

$$\nu = \frac{3}{4}R(Z - 1)^2.$$

where ν = Frequency of the K line.

Z = Atomic number of the element.

R = Rydberg's constant.

The corresponding wavelength (λ) is obtained from the relation:

$$\lambda = \frac{c}{\nu}$$

where c is the velocity of light.

From this it follows that once the frequency of the K line has been established, the atomic number of the element may be calculated. A general discussion of techniques and a comparison with normal optical methods will be found in G. von Hevesy¹, G. L. Clarke² and W. T. Sproull³.

X-ray methods, although physically rather complex, offer many advantages. Each element present emits its x-ray spectrum regardless of the state of chemical aggregation, a point of particular cogency in cases where isolation of the element (e.g. a rare earth) would be difficult by chemical methods.

Identification is greatly assisted by the relative simplicity of Moseley's law and the form of the observed spectra. Four to six lines of a spectrum, coupled with observation of their relative intensity, are sufficient to determine an element⁴, which may be contrasted with the very complex optical spectra.

The x-ray emission spectra may be excited by making the element the target of an x-ray tube as was done in Moseley's original researches. The difficulty inherent in using standard machines for this purpose and the possibility of selective volatilization of elements under intense heating, have led to development of the secondary fluorescence method in which the spectrum is excited by exposure to hard x-rays. The sample may then be placed within the x-ray tube, but out of the cathode stream, or even outside the tube altogether. This last method is very convenient, but suffers from a great reduction in the intensity of the emitted spectrum.

¹ *Chemical Analysis by X-rays and its Application*, (McGraw-Hill, New York), 1935.

² *Applied X-rays*, (McGraw-Hill, New York), 1940.

³ *X-rays in Practice*, (McGraw-Hill, New York), 1938.

⁴ C. E. Eddy, T. H. Laby and A. H. Turner, *Proc. Roy. Soc.*, A124, 1929, p. 249.

J. S. Stevenson¹ describes the determination of niobium (columbium) in pyrochlore ores using the sensitive Geiger counter to detect the weak Nb K_{α} and K_{β} emission when exposed to tungsten radiation.

Quantitative Determination of Elements

Chemical and spectroscopic analyses are generally more sensitive quantitatively than the x-ray method. J. S. Stevenson, in the paper referred to above, describes an x-ray technique based on the intensity of the K_{α} emission line. Standard mixtures containing known amounts of niobium were prepared and exposed in turn to the exciting rays, the K_{α} intensity being measured by the Geiger counter apparatus. A graph showing variation of intensity with concentration was prepared from which, by interpolation, the Nb concentration in ores could be deduced. Even though the greatly improved Geiger counter detectors and the focusing spectrograph are helping to improve x-ray recording methods, there remain fundamental difficulties in relating the quantity of an element present with the intensity of its x-ray spectra, which arise from the modifying effects of other elements present. A further practical difficulty occurs with light elements due to the long wavelengths of the K spectra which require vacuum spectrographs for their detection.

MINERAL IDENTIFICATION BY POWDER DIAGRAM

So few cases exist where different minerals give the same powder pattern, that a mineral may be identified by detailed comparison of a good powder diagram with a selection of diagrams of likely minerals taken under similar conditions. Such a method is rather cumbersome in general, with so many different camera designs and recording techniques. J. D. Hanawalt, H. W. Rinn and L. K. Frevel² introduced a very useful system of indexing powder diagrams in terms of the plane spacings and intensities of the most prominent lines, which has since been expanded by the *American Society for Testing Materials* to include several thousand compounds, among which are many of interest to mineralogists. In the *A.S.T.M.* card index each compound is represented by three cards, one for each of the three strongest reflections, listed in order of plane spacings. The remainder of the lines for that compound and their relative intensities are entered on each card. The search for a mineral may thus be carried out systematically once its powder diagram has been studied.

Short lists of minerals of special interest may be found in technical literature and in text books, among which may be mentioned

¹ *Amer. Min.*, 39, 1954, p. 436.

² *Ind. Eng. Chem. Anal.*, 10, 1938, p. 457.

G. A. Harcourt¹ (ore minerals), G. W. Brindley² (clays) and more recently, H. W. van der Marel³; the latter includes more than thirty powder photographs of clays, including mixtures of components. The powder photographs of the chemically identical series nacrite-dickite-halloysite-kaolinite (Pl. 21) show well-marked differences.

IDENTIFICATION OF MIXTURES

In a true mixture, as opposed to a solid solution, each component, if present in sufficient concentration, gives rise to its own powder pattern and identification consists in an extension of the above procedure, one component at a time being identified by comparison with known patterns, its system of lines eliminated, and the remainder analysed for further members. An upper limit to the number of components which may be dealt with is set by the crowding of the lines and the possibility of overlapping. The opening out of the diagrams which larger diameter cameras and longer wavelengths produce, assists in this respect. A mineral present in too small a concentration will not record on a powder diagram. If a single fragment of such a mineral can be extracted from the mixture, as a result of examination under the microscope, its identity may be confirmed by comparing a rotation photograph with a suitable powder diagram⁴.

Clay mineral mixtures afford an interesting example of the combination of physical, chemical and x-ray methods. The powder diagrams are generally less sharp than those for more well formed minerals and owing to the large cell dimensions have an abundance of lines crowded into one quadrant (Pl. 21). The important reflections for the purpose of identification are those from basal layers of tetrahedral Si-oxygen or Al-oxygen groups, with spacings up to about 20Å.

The intensities of these basal reflections may be increased by the aggregate technique of specimen preparation introduced and used by G. L. Clarke, R. E. Grim and W. F. Bradley⁵, G. Nagelschmidt⁶ and others. The small plate-like crystallites are orientated to lie parallel to each other by slow sedimentation from suspension or centrifuging against a glass plate. A powder specimen from such an aggregate shows greatly enhanced basal reflections.

Difficulties remain, however, due to similar basal spacings of

¹ *Amer. Min.*, **27**, 1942, p. 63.

² *X-ray Identification and Crystal Structures of Clay Minerals*, (Mineralogical Society, London), 1951.

³ *Soil Sci.*, **70**, 1950, p. 109.

⁴ E. G. Steward, *Analyst*, **79**, 1954, p. 173.

⁵ *Z. Krist.*, **96**, 1937, p. 322.

⁶ *J. Sci. Instr.*, **18**, 1941, p. 100.

vermiculite, chlorite and montmorillonite at 14Å. G. F. Walker¹ has described a standard procedure by which they may be distinguished. Montmorillonite swells when treated with glycerol to give a spacing of 17·7Å, a method introduced by D. M. C. MacEwan². Vermiculite shrinks when leached in ammonium salt solution to 11Å, while chlorite does not respond to either treatment. Accordingly, if a mixture of these minerals is treated with glycerol and ammonium salt solution, basal spacings of 11, 14 and 17Å indicate the separate constituents. Selective removal of montmorillonite by an acid solvent and the destruction of kaolinite and halloysite by heat treatment, are mentioned by D. M. C. MacEwan³ in a general discussion of difficulties encountered in clay analysis. Chemical and optical methods are not capable of achieving these results.

QUANTITATIVE ANALYSIS OF MIXTURES

The concentration of a given constituent may be estimated from the intensity of its powder lines, but owing to difficulties of a fundamental nature⁴ the method is empirical. Standard mixtures containing the same minerals are prepared and the variation of the intensity of certain lines in the powder pattern with percentage composition measured. A powder diagram of an unknown mixture may then be taken under the same conditions and composition determined by interpolation. As a general figure, an estimate to within 5%, using a direct comparison of intensities by eye, or, if the line densities can be determined by a microphotometer, to within 1%, may be made. H. P. Rooksby⁵ was able to detect 0·1% of CaO in magnesia, and W. Hughes and H. Smith⁶ investigated mixtures of rutile and anatase by this method. Rough estimates only (to within $\pm 20\%$) of the minerals in soil colloids are reported by G. Nagelschmidt⁷.

The minimum quantity of a given mineral which may be detected varies greatly and depends upon the degree of crystallinity, orientation, symmetry and diffracting power of the crystallites. Quartz in concentrations of only 0·2% can be detected readily, while about 1% of calcite is required. Less symmetrical crystals, like monoclinic gypsum, can be detected only if more than 5% is present. Use of a strictly monochromatic beam and an evacuated camera reduces the general background which otherwise obscures weak reflections.

¹ *Nature*, **164**, 1949, p. 577.

² *Nature*, **154**, 1944, p. 577.

³ *Research*, **2**, 1949, p. 459.

⁴ G. W. Brindley, *Phil. Mag.*, **36**, 1945, p. 347.

⁵ *Analyst*, **70**, 1945, p. 166.

⁶ *Analyst*, **77**, 1952, p. 179.

⁷ *Journ. Agric. Sci.*, **29**, 1939, p. 477.

MIXED CRYSTALS

Many examples occur in mineralogy of mixed crystals. Between two end members a continuous range of compositions is found, the unit cell changing slowly along the series, and the corresponding powder diagrams vary continuously, both as regards line positions and intensities. Sensitivity of the powder method in following small changes of cell size and shape has been utilized in the case of monoclinic pyroxenes related to diopside. Table 26, from a paper by H. Kuno and H. H. Hess¹, shows the small but systematic change of lattice parameters in the series of minerals studied. Powder diagrams of each member were used to determine these quantities to the required degree of accuracy. It is suggested that by interpolation the Ca-Mg-Fe content of a mineral in this series could be inferred.

TABLE 26
VARIATION OF LATTICE CONSTANTS WITH COMPOSITION (KUNO AND HESS).

Lattice constant	Pigeonite Ca ₈ Mg ₆₄ Fe ₂₈	Diopside Ca ₄₀ Mg ₄₇ Fe ₄	Ferrosalite Ca ₃₀ Mg ₁₇ Fe ₂₈	Hedenbergite Ca ₄₄ Mg ₈ Fe ₁₀
<i>a</i>	9.692 Å	9.750 Å	9.804 Å	9.854 Å
<i>b</i>	8.917 Å	8.930 Å	8.980 Å	9.024 Å
<i>c</i>	5.239 Å	5.249 Å	5.259 Å	5.263 Å
β	71° 27'	74° 10'	74° 46'	75° 40'

The structural changes accompanying replacement of Na by K in a series of synthetic high temperature alkali-feldspars have been investigated using the powder method². Unit cell edges and angles were measured and plotted against composition. Although there is a discontinuous change from the triclinic to the monoclinic form, most of the parameters show a continuous variation. Only α , γ and d_{111} show marked changes at the transition.

NEW MINERALS

In difficult cases, final identification of a mineral can only be made after recourse to a combination of many techniques including single crystal methods. G. F. Claringbull and M. H. Hey³ have shown how optical, x-ray and chemical methods combine to establish

¹ *Amer. Journ. Sci.*, **251**, 1953, p. 741.

² G. and J. D. H. Donnay, *loc. cit.* (see p. 488).

³ *Miner. Mag.*, **29**, 1952, p. 841.

the nature of a new mineral, sinhalite (MgAlBO_4), previously mistaken for olivine.

PARTICLE SIZE ANALYSIS

Powder diagrams show sharp, smooth diffraction arcs only for a limited range of crystallite sizes (between about 10^{-5} and 10^{-3} mm.). For particles of mean diameter greater than 10^{-3} mm., the arcs become spotty due to Laue diffraction; below 10^{-5} mm., the lines are broadened, there being too few atomic layers within the crystallites. Both extremes have been used to estimate grain sizes^{1, 2}. Unfortunately, in the very case (clays) where such information would be useful, other causes, such as irregularity of structure, give line broadening. The electron microscope offers many advantages over these indirect methods³.

GEOLOGICAL PROCESSES

X-ray methods open up possibilities of studying the origin, modes of formation, thermal history and metamorphosis of mineral deposits. The role of metals during crystallization in the cooling magma is discussed briefly by J. M. Bijvoet⁴. W. S. Mackenzie⁵ describes the transition of anorthoclase from a triclinic lattice at normal temperatures, to a monoclinic form at high temperatures, and suggests that the cross-hatched appearance of this mineral may be due to crystallization from lava at high temperature in the monoclinic form and the change to a triclinic form on cooling.

M. L. Keith and O. F. Tuttle⁶, in a study of the inversion temperature of quartz from different environments, propose that the observed differences may give significant information regarding thermal aspects of geological processes. The effect of the environment on the inter-planar spacings in calcite included in iron ores, reported by K. W. Andrews⁷, is thought to be due to the solid solution replacement of Ca by Mn and to some extent by Mg and Fe.

Powder specimens may be prepared from as little as 0.1 g. of material. Such fine sampling described by G. Brown⁸ may be used to follow mineralogical changes occurring in localized centres of soil formation, as opposed to sampling whole horizons.

¹ H. P. Rooksby, *J. Roy. Soc. Arts.*, **90**, 1942, p. 673.

² *Op. cit.*, p. 5, A. Guinier, (1952).

³ See Chapter XIV.

⁴ *Op. cit.*, p. 187.

⁵ *Amer. Journ. Sci.*, Bowen Vol., 1952, p. 319.

⁶ *Amer. Journ. Sci.*, Bowen Vol., 1952, p. 203.

⁷ *Miner. Mag.*, **29**, 1950, p. 85.

⁸ *Journ. Soil Sci.*, **4**, 1953, p. 229.

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CHAPTER XIV

ELECTRON MICROSCOPY OF MINERAL PARTICLES

R. J. Bird, B.SC., A.INST.P. and L. O. Freeman, M.SC.,
PH.D., A.R.I.C.

Introduction—Principles—Range and Limitations—Apparatus—
Techniques—Specimen Preparation—Preparation of Supporting
Films—Dispersion and Mounting of Powders—Shadow Casting—
Particle-Size Analysis—Surface Replicas—Operational Techniques
—Adjustments and Precautions—Electron Microdiffraction—
Applications—Natural Mineral Particles; Industrial—Solid Sur-
faces—Future Trends—Selected Bibliography.

INTRODUCTION

THE optical microscope has played a major part in the petrography of sediments; in studies of their lithology and mineralogy it is likely so to continue. It is, however, limited to useful magnifications up to about 1000 diameters and is of little use in studies of particle detail much less than micron size. The electron microscope, using a beam of electrons instead of light, has vastly increased the range of useful magnifications available to the microscopist, who may now study detail down to a few tens of Å units in size.

In application, the instrument is to some extent limited by poor penetrating power of electrons in solid matter, but it has already had an enormous influence on many branches of science. In petrology, it has the further disadvantage for diagnostic work of being insensitive to colour and refractive index. In this field, therefore, it must be regarded as supplementary to, rather than superseding, a visible light instrument.

Because of the very poor penetrating power of electrons, specimen requirements for electron microscopy are very different from those for visible-light microscopy. A high degree of skill and ingenuity are often required to achieve good results, and methods are still very much in a state of development. It is still impracticable to

produce petrological sections thin enough for electron microscopy and this particular problem is indeed formidable.

The use of the instrument in sedimentary petrography has so far been confined mainly to examination of finely divided particulate matter. It has been used principally in studies of argillaceous deposits, whose particles are generally too small to be revealed by the optical microscope.

Probably more use has been made of the electron microscope in connexion with mineral particles for industrial purposes. These include cements, ceramics, pigments and fillers for use in such materials as rubber, plastics and paint. Some applications of electron microscopy to the determination of mineral particles are given later in this chapter (p. 516).

Though not strictly microscopy, a valuable feature of electron microscope technique is provision for examination of electron diffraction patterns. Suitable specimens of crystalline matter give a pattern characteristic of that particular substance and this can lead to positive identification.

PRINCIPLES

The underlying principles of electron microscopy emerged some years ago. L. de Broglie put forward the idea of a wavelength associated with moving particles¹ and experimental evidence of this was subsequently obtained by C. J. Davisson and L. H. Germer². About the same time it was shown by H. Busch that it was possible to focus a beam of electrons by means of a magnetic field³.

The wavelength associated with a particle is given by the relation:

$$\lambda = h/mv$$

where h is Planck's Constant,

m is the mass of the particle (g.),

v is the velocity of the particle (cm.sec.⁻¹).

For an electron which has been accelerated through a potential difference of V volts this becomes:

$$\lambda = \frac{150}{\sqrt{V}} \text{ \AA.}$$

Thus for an accelerating potential of a few thousand volts, the associated wavelength is a fraction of an Ångstrom unit and the utilization of such wavelengths in a microscope would be expected to lead to very high resolving powers.

¹ Dissertation, (Masson, Paris), 1924; *Phil. Mag.*, **47**, 1924, p. 446.

² *Phys. Rev.*, **30**, 1927, p. 707.

³ *Ann. Phys.*, **81**, 1926, p. 974.

Focusing a beam of electrons may be effected by a radially symmetrical magnetic field oriented parallel to the axis of the beam. The electrons tend to follow helical paths through the field (strictly helical paths in an axially uniform field) and there is additionally a rotation of images formed in this manner.

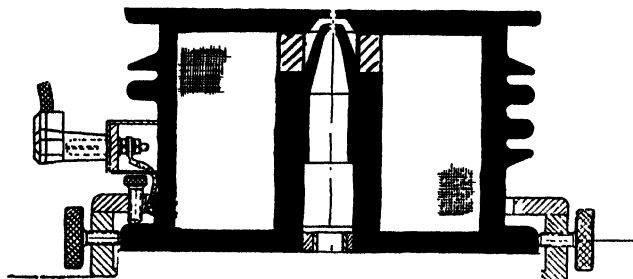


FIG. 79. Cross-section through Objective Lens of Metropolitan Vickers E.M. 3 Microscope.

The effective focal length of a magnetic lens varies inversely as the square of the magnetic field. Thus, where the field is provided by means of a solenoid, the focal length may be varied by altering the energising current. This property of electromagnetic electron lenses greatly facilitates focusing and change of magnification in the electron microscope. Focal lengths required for electron microscopy are of the order of a few mm., and to achieve required field-strengths, it is necessary to concentrate the flux generated by the solenoid into a very small gap by means of iron shrouds and accurately-machined pole pieces. A typical arrangement is illustrated in Fig. 79, showing a cross-section through the objective lens of the Metropolitan Vickers E.M. 3 microscope.

A beam of electrons may also be focused by means of a suitably-shaped electrostatic field such as that provided by a spaced system of circular apertures maintained at different potentials. Electrostatic lenses are simple in construction and have certain advantages. They are, however, sensitive to the presence of dust particles on the critical edges. Particularly where particles are of insulating materials, they may distort the field and detract from image quality. Electrostatic lenses have not found much application in high-performance commercial instruments.

Both electromagnetic and electrostatic lenses are, in the terminology of light-optics, simple lenses. As such, they exhibit marked aberrations, the most important being chromatic and spherical

aberrations and astigmatism; they may only be used with advantage at what, by ordinary standards, are very low angular apertures.

Whereas image-contrast in the visible light microscope depends mainly on a combination of selective absorption and scattering due to differences of refractive index, in the electron microscope scattering itself is the most operative effect. Absorption is, in fact, undesirable, for the energy imparted to the specimen may raise its temperature sufficiently to cause serious damage and the charge acquired by an absorbing specimen may also lead to its disruption, by reason of electrostatic forces set up.

In passing through a specimen, electrons may be scattered elastically and suffer only change of direction; or they may be scattered inelastically, losing energy, thus changing their associated wavelength. In a wide aperture, highly corrected optical system, most scattered radiation is collected and used to build up the image, but in the electron microscope, by reason of high spherical aberration and small aperture, elastically scattered electrons, for quite small deviations, are either displaced from image-point or lost altogether. Chromatic aberration operates to defocus inelastically scattered (longer wavelength) electrons.

A complete electron microscope has a layout somewhat similar to that of the visible light microscope. In its simplest form it has three lenses fulfilling the familiar functions of condenser, objective and projector or eyepiece. In place of a light source, there is usually a tungsten filament emitting electrons, accelerated by suitable high potential differences and directed as a stream through the instrument. In place of the ground glass screen of a visible light microscope system, there is a fluorescent screen to reveal the electron image, but in both types of system, photographic plates may be used to record images produced directly. As a matter of convenience, the electron optical path is usually directed vertically downwards instead of vertically upwards. A diagrammatic representation of a three-lens electron microscope and analogy with the visible light microscope, are given in Fig. 80. In the more recent instruments there has been a trend towards the use of more than three lenses, with advantages to be discussed later (p. 505).

RANGE AND LIMITATIONS

In spite of the very small angular apertures (of the order of 10^{-3} radians) employed in electron microscopes, very high resolving powers are attainable. This is due to the extremely small wavelength associated with electrons of the energies used in electron microscopy. Application of the familiar expression for the limiting resolution of a microscope objective, as set by diffraction effects, to 50kV

electrons, the associated wavelength of which is 0.055 \AA , taking the numerical aperture to be 0.005 , leads to:

$$d_{\min} \approx \frac{\lambda}{2 \times \text{numerical aperture}} \approx 5 \text{ \AA}$$

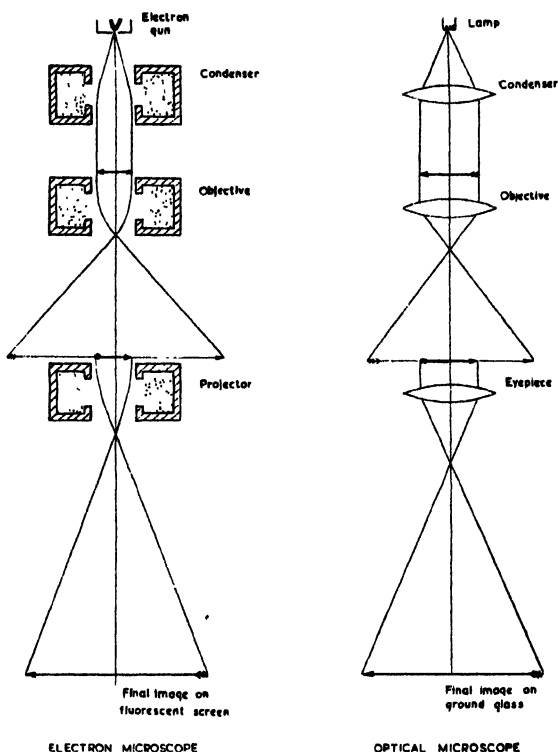


FIG. 80. Diagram of 3-Lens Electron and Optical Microscopes.

In practice, lens aberrations are not negligible and the diffraction limit of resolution is never quite attained. Decreasing aperture reduces the effect of aberrations, spherical, chromatic and astigmatism, but increases the diffraction effect; the best compromise aperture is sought, having regard to expected aberration coefficients.

Specially prepared microscopes have actually achieved resolutions approaching 5 \AA and little further improvement of resolution can be expected with the present type of instrument. As to the future, some work has been directed towards correction for spherical

aberration, the most important of the aberrations in electrostatic lenses; this would put up the permissible aperture and ideas have been entertained of achieving by this means a resolution of the order of 1Å.

With a modern high-resolution instrument in good adjustment, useful magnifications of up to $\times 100,000$ may be employed. At the other end of the scale, magnifications down to about $\times 1000$ are commonly available and in some instruments it is possible to reduce magnification down to as little as about $\times 100$. It is often helpful to be able to scan a specimen at low magnification before examining it locally at a much higher magnification.

So far, the effect of the sample on the performance of the instrument has been neglected. The outstanding limitation of the electron microscope lies in its poor penetrating power of electrons for solid matter; therefore, in normal transmission work, it is essential to keep specimen-thickness down to small dimensions if useful results are to be achieved. As a rough guide, minimum resolvable detail in a specimen is about $\frac{1}{10}$ its thickness. This refers specially to thin sections of organic matter, but none the less serves to illustrate the point. It follows that in examination of particulate matter and any non-self-supporting specimen, the supporting film, used in place of the glass slide of optical microscopy, must be extremely thin.

The penetrating power of electrons can be increased by use of higher accelerating potentials and something can be done by this means to increase permissible maximum specimen thickness. There are, however, serious disadvantages in raising voltage; generation and stabilization become more of a problem and x-ray hazards increase. With the faster electrons also, magnification provided by the lenses is decreased. In commercial microscopes the maximum voltage provided is 100 kV.

The limited penetration of electrons means that direct transmission electron microscopy is restricted to a study of particulate matter or sections of thickness depending on the material, but not in excess of about 0.2μ and preferably much less. The technique may be extended to the study of surface-contour detail of solids by preparation and examination of suitably thin casts or 'replicas' of surfaces made with suitable material.

More recently, a reflection technique has been developed for direct examination of solid surfaces; it amounts to viewing the specimen surface at a low grazing angle. Detail seen is subject to severe perspective effects, which may make appreciation of true shape somewhat difficult. This technique, applicable only to electrically-conducting surfaces, gives resolution far short of that realized in normal transmission work. It has, however, proved useful in metallurgical work and although not yet utilized in mineralogy,

there may conceivably be applications in this direction. A number of existing microscopes may be used for this type of examination after slight modifications, which consist essentially of tilting the electron gun and condenser unit and arranging an almost vertical specimen holder so that both 'illuminating' and viewing directions make small angles with the specimen surface.

APPARATUS

The complete electron microscope is a complex piece of apparatus and this complexity stems from two main sources. The first is the need to operate in a high vacuum enclosure, such as will keep gas-scattering of the electrons down to a low level, a pressure of the order of 10^{-5} mm. of mercury being employed in practice. A vacuum of this quality is produced with a vapour diffusion pump, usually of the oil type, although sometimes mercury is used as the working fluid. The vapour pump cannot work against atmospheric pressure, however, and it is necessary to 'back it' with a mechanical pump producing a vacuum of the order of 10^{-1} mm. of mercury.

The body of the microscope has to be vacuum-tight in construction, yet provide for alignment motions and stage controls. This means that a variety of vacuum seals must be built into the instrument. There must also be vacuum-tight ports for insertion and removal of plates and specimens. Some instruments have vacuum locks for this purpose, only a small quantity of air being admitted at each change. In others the complexity of locks is avoided and at each change the whole instrument is opened to the atmosphere, then re-evacuated.

The other main source of complexity lies in lack of correction in electron lenses. Such lack of chromatic correction means that the equivalent of monochromatic illumination must be employed, *i.e.* wavelength of the electrons must be maintained constant; in other words, the accelerating potential must be highly stabilized. A stability of at least 1 part in 20,000 is desirable for a magnetic microscope.

In order to secure and maintain accurate focusing, the lens currents of an electromagnetic microscope must also be highly stabilized. A figure of 1 part in 50,000 is aimed at in some instances. Provision of high current stability at low voltage is, however, much less of a problem than that found in the high-voltage stabilization. In some instruments, accumulators are used for stable lens supplies; in others, electronic stabilization is employed.

Electron microscopes were first made commercially available in Europe in 1939, with the Siemens instrument designed by B. von Borries and E. Ruska. In the United States the RCA Model B was later introduced

(1940); Metropolitan-Vickers (England) produced their E.M.I. Model in 1947. All these microscopes were of the electromagnetic type, as have been a majority of later high-resolution instruments. There have been a few electrostatic microscopes and partly electrostatic microscopes made in Germany, France and Switzerland, but these have not generally equalled the other type in performance and are better suited for comparatively low-power routine work.

For less exacting semi-routine applications, simplified magnetic microscopes with limited working magnification have also been produced. One by R.C.A. has permanent magnet lenses. The Metropolitan-Vickers E.M.4 and the Phillips E.M.75 are also designed for this work, the latter being remarkable in that it contains no thermionic valves. It is probably true to say, however, that simplified instruments are still less numerous than the more versatile high-performance models.

Some earlier magnetic microscopes were capable, under good conditions, of resolution not far short of that of instruments produced at present. There has latterly, however, been a considerable improvement in reliability and ease of manipulation. On the vacuum engineering side, sliding ground joints and flat rubber seals have given way to flexible metal bellows and simple rubber ring seals; with the electrical equipment there has been a trend towards replacement of expensive and bulky low-frequency high-voltage generators by radio-frequency apparatus, utilizing standard components; this makes for cheapness and rapid servicing, and such circuits facilitate a high level of output voltage stability.

In more recent electron microscopes there is a tendency towards incorporation of a greater number of lenses; by this means it is possible to achieve a given maximum magnification with a shorter instrument and this makes for improved rigidity and ease of manipulation; it also facilitates working at low magnifications, which is often desirable. Magnifications down to $\times 1000$, in some cases well below, are available simply by lens switching, whereas in simpler instruments it is necessary to change lens pole-pieces for magnifications below about $\times 3000$. With the extra lenses it is also possible to reduce distortion at low magnifications. A further advantage of the multilens instrument is the ease with which it is possible to produce diffraction patterns from selected areas of the sample; the change from microscopy to diffraction can be made in a few seconds. Such diffraction patterns can be of great help in identification of crystalline materials.

Pl. 22 shows one modern high resolution microscope. This, the Metropolitan-Vickers Model E.M.3, is a four-lens instrument giving direct magnification from about 700 to 60,000 times. Maximum accelerating voltage is 80 kV. The column has conventional vertical mounting and is placed on a desk-type support with the lens-current supplies and controls built into the wings. The radio frequency high-voltage generating equipment is contained in the separate cabinet. There are no vacuum locks in the instrument, which is completely let up to atmospheric pressure whenever a change of specimen or photographic plates is required. With powerful pumps and a fairly small

pumped volume, the time taken to achieve a working vacuum is reasonably short. With the latest version, the E.M.3A, a resolution of 20\AA is attainable.

Another instrument is the Phillips E.M.100. It contains five lenses, although not more than four are used at any one time. Instrument magnifications from 600 to 90,000 times are available and accelerating voltages up to 100 kV. The resolving power claimed is 'better than 20\AA '. This microscope incorporates a number of novel features. The actual column slopes upwards towards the observer at the front and terminates in a glass fluorescent screen on which the image is displayed, as in normal cathode ray tube practice. Images are recorded on a 40-exposure film camera, racked into the electron beam as required. Rapid examination of successive specimens is facilitated by provision of a specimen lock. The complete instrument including pumps, power racks and the low frequency high voltage equipment is contained within the one console.

Continuing the trend towards more lenses and greater versatility in electron microscopes, a Japanese instrument known as J.E.M.5 has six lenses, will give magnifications from $\times 80$ to $\times 100,000$, and may be used for reflection work without mechanical modification. This is made possible by built-in deflector coils which direct the beam on to the sample at a suitable angle; there is also a built-in specimen heater for examination at high temperatures. The resolution claimed for this instrument is 15\AA .

Finally some mention should be made of the Siemens Elmiskop I, a five lens microscope recently introduced, and of the Metropolitan Vickers EM6, another five lens model soon to be available. These instruments are of very high, rather similar performance, a resolving power of 15\AA or better being guaranteed for production models, whilst specially prepared models of each have achieved resolutions in the region of 5\AA . Each has an advanced design of 'illuminating system' incorporating a double condenser lens, and the stabilization of supplies is taken to a very high level. For the EM6 accelerating voltage stability is $1:10^5$ and objective lens current stability is $1:50,000$. In both instruments there is provision for rapid changing of objective aperture discs during operation. This is of great importance for contamination of these apertures is now known to be rapid, and highly detrimental to performance when working at this level of resolution. The EM6, though not the Elmiskop I, has built-in beam deflecting apparatus to facilitate reflection microscopy.

TECHNIQUES—SPECIMEN PREPARATION

(a) *Preparation of supporting films.* Much of the technique concerned in electron microscopy of sediments relates to examination of fine particulate matter. The particles must be suitably supported in the microscope, but because of the extremely small penetrating power of the electrons, it is permissible to use only a very thin membrane for this purpose. Suitable membranes are commonly prepared from

collodion and from 'Formvar'¹ (polyvinyl formal). To facilitate handling and insertion in the microscope, these are in turn usually mounted on a small circular grid of 200-mesh gauze or, less commonly, on a thin metal disc with a single central hole. Various means have been devised for preparing and mounting these plastic membranes; all have one feature in common, viz. use of a water surface on which to keep the membrane extended during manipulation.

In the case of collodion, the film may be formed by taking a solution (about 0.5% w/v) in some suitable solvent, e.g. amyl acetate, and allowing a few drops to fall on to a clean water surface. The solution spreads rapidly to a thin layer, from which the solvent evaporates in a few seconds, leaving the solid membrane floating on the surface. The amount of solution required to produce the right thickness varies according to conditions and is best found by trial and error. The appearance of the cast film is a good guide; it should be too thin to show interference colours and be visible mainly as a small change of reflectance of the water surface.

Mounting the membrane on grids or discs may be achieved by dropping the latter on to the membrane in a suitable cluster, then pressing a piece of glass (e.g. microscope slide) gently down over it. The edges of the membrane are folded over the back of the microscope slide, which is then lifted clear, bringing with it grids plus membrane, in that order, adhering to its underside. The slide is turned over and dried, after which the coated grids may be broken out for use as required. Another method of coating grids is to submerge them in a water trough on a piece of heavy gauze and then to raise them up and out through the floating film. Again, the membranes may be formed by coating a slide with a thin film of the collodion or Formvar, which can be done either by dipping or flooding, and draining with a solution of suitable strength, usually about 0.25%. When dry, the film is scored with a sharp point into small squares and floated off on to a water surface by gently submerging the slide at a shallow angle with film uppermost. Separation of the film is greatly assisted by first breathing on it. Following this, the procedure is as before. This method is particularly valuable for Formvar, which cannot be spread on water from some of its best solvents.

Supporting membranes of collodion or Formvar are satisfactory in most applications of electron microscopy to the study of mineral particles and they have the great advantage of being easy to prepare. In some applications, however, a plastic support is unsuitable; chemical resistance may be required or a greater degree of stability to heat, when films of many other materials have to be employed.

¹ Obtainable from Shawinigan Products Corp., New York.

These include the metals aluminium and beryllium^{1, 2, 3}, silica⁴, silicon monoxide⁵ and most recently, carbon⁶. With all these materials the film is formed by deposition from the vapour phase under high vacuum. A very smooth surface is required on which to form the deposits, but it must also be one from which the film may be separated and mounted.

Metal films have been successfully formed on a surface of glycerine⁷, which has a suitably low vapour pressure. They may be freed from traces of glycerine by water washing. Silicon oxides may be deposited on a plastic surface (e.g. polystyrene) and freed by solution of the latter in ethylene bromide, but the films are difficult to see and handle because they do not float; they often show a strong tendency to curl. Sometimes it helps to transfer pieces of film to another bath containing a layer of benzene over a layer of ethylene glycol, where they are held flat satisfactorily at interface.

Another method used for production of both metal and silicon oxide films, is to form them on Formvar- or collodion-covered microscope slides. The composite films may sometimes be floated off on water, mounted on grids and then solvent treated to remove the plastic; otherwise films are freed by solution of the plastic. This procedure has been utilized in preparation of carbon films, with a difference in choice of plastic substrate, a more readily soluble plastic, polybutyl methacrylate, being employed. Composite films usually float on a water surface. By these vacuum evaporation methods, supporting films of a thickness 20 to 50 Å may be prepared. Of these non-plastic materials for supporting films, carbon has lately come to the fore. It is easy to prepare, is strong and resistant to the heating effect of the electron beam and has no discernible structure. The thinnest films are almost invisible in the microscope.

(b) *Dispersion and mounting of powders.* In the examination of the powder in the electron microscope, the choice of method of specimen preparation depends partly on the information required and partly on the powder itself. Generally the shape and size of ultimate particles is the information sought and in this case the best attainable dispersion is employed with advantage; this applies not only to particle-size analysis but to diagnostic work; also where some constituent might otherwise remain unnoticed. Sometimes the state

¹ F. E. Carpenter and J. A. Curcio, *Rev. Sci. Instr.*, **21**, 1950, p. 675.

² N. Hast, *Nature*, **162**, 1948, p. 892.

³ W. Kaye, *Journ. Appl. Phys.*, **20**, 1949, p. 1209.

⁴ C. H. Gerould, *Journ. Appl. Phys.*, **18**, 1947, p. 333.

⁵ C. Haas, *Journ. Amer. Ceram. Soc.*, **33**, 1950, p. 353.

⁶ D. E. Bradley, *Brit. Journ. Appl. Phys.*, **5**, 1954, p. 65.

⁷ N. Hast, *loc. cit.*, 1948.

of aggregation of the particles is of interest, perhaps in connexion with some particular industrial application, when it may be a difficult problem to employ the right degree of dispersion. In such event it is a better plan, if possible, to examine the finished product, paint, rubber, etc., by thin sectioning; such procedures, however, are not directly related to sedimentary petrography and are therefore not pursued further here.

The exact procedure for production of the dispersed specimen will vary with the nature of the material. Water-wet materials may be made into dilute water-suspensions with perhaps an addition of some suitable surface active agent for minimizing flocculation. Small quantities of the suspension are then transferred to the prepared grids. The suspension should be thoroughly agitated up to the moment of sampling, in order to avoid possible loss of larger particles by sedimentation.

Various methods have been tried for loading the grids. A small drop may be put down and allowed to dry naturally, but in this way flocculation is often troublesome. Alternatively, the suspension may be sprayed¹ and the grid loaded with a number of microscopic droplets, each containing only a few particles. This reduces drying time and generally tends to give better samples. Where particle concentration is low enough and evaporation rapid, the sample material may be deposited as separate dry particles. Another method is to chill the grid below 0°C before applying a drop of the suspension; then after a very short time interval that part which is still liquid is withdrawn, a thin frozen layer of the suspension remaining on the support. This may be allowed to dry naturally or, better still, it is freeze-dried, which effectively preserves the state of dispersion of the particles.

Dry powders may be well dispersed by working up as a paste in a suitable viscous oil, *e.g.* boiled linseed or poppy-seed oil. These have very good wetting power which is highly desirable in this application. The ground paste is greatly diluted with an oil-solvent which will not harm the collodion or Formvar substrate and drops of the suspension are spread on prepared grids. When the solvent has evaporated and all particles are settled on the substrate, gentle solvent washing is required to remove the small amount of oil present. There is never any certainty that some particles are not lost in this washing process, but the method has been widely employed.

In the case of a dry powder, it is often satisfactory to disperse it in a solution of collodion or Formvar. Thorough dispersion can be achieved by mulling in a viscous solution on a glass plate. The mix is then greatly diluted with pure solvent and spread out to a thin

¹ R. C. Backus and R. C. Williams, *Journ. Appl. Phys.*, 21, 1950, p. 11.

layer on the plate. In a few seconds the solvent evaporates leaving the dispersed particles set in a thin plastic film. With practice the resultant film thickness can be made similar to that for normal supporting membranes. The film with particles embedded in it can be floated off on water and collected on grids in the usual way. Alternatively, the dilute suspension may be spread directly on the water surface and collected as before when dry.

Where vigorous dispersion is not desirable, such as in investigating aggregation of fine particles, dusting methods are available. In one such method the powder is contained in a shallow vessel. A high alternating potential of several thousand volts is applied to an electrode positioned above it and maintained in mechanical vibration. The powder is agitated sufficiently to cause it to dust over suitably placed microscope grids¹.

A very simple way of depositing a sample of fine powder on a supporting film, although not necessarily a truly representative one, is as follows². A quantity of the sample is taken in a test-tube and shaken vigorously; the tube is then inverted and the bulk of the material rejected. The inverted tube is quickly placed over the specimen grid and the air-suspended remainder is allowed to settle. The latter part of this technique is a satisfactory method of sampling airborne dust where the concentration of particles is fairly high. In cases where it is required to examine a dust of low particle concentration, it is necessary to employ some form of precipitator through which large quantities of air may be slowly passed. One type of precipitator consists of a small chamber down the centre of which is mounted an insulated wire. This wire is heated by the passage of an electric current and, as the dust-bearing air passes, the thermal energy imparted to the particles causes them to collect on the walls. Microscope specimen grids are suitably placed to receive a representative deposit. In some precipitators electrostatic forces are employed. The air is passed between concentric conductors, one of which has microscope grids set in its surface. When a potential of several thousand volts is applied, the dust is deposited on the conductor surfaces and representatively sampled by the grids^{3, 4}.

(c) *Shadow casting.* To make the particles more readily visible and to give information on the third dimension, it is sometimes useful to 'shadow-cast' microscope specimens with a directional deposit of metal⁵. The deposit must be thin enough to transmit a reduced

¹ H. C. O'Brian, *Journ. Appl. Phys.*, **16**, 1945, p. 370.

² M. Frey, *Bull. Soc. Chim. Fr.*, **17**, 1950, p. 1064.

³ M. L. Fuller *et al.*, *Journl Appl. Phys.*, **15**, 1944, p. 201.

⁴ G. Riedel, *Kolloid Z.*, **103**, 1943, p. 228.

⁵ R. C. Williams and R. W. G. Wyckoff, *Journ. Appl. Phys.*, **17**, 1946, p. 23.

but substantial part of the electron beam. The technique is of use only with particles resting on, as distinct from embedded in, the supporting film and is carried out in a high vacuum chamber. The metal to be used is loaded on to a tungsten filament suitably placed relative to the sample, and when the filament is heated by the passage of an electric current, the metal evaporates. Provided the vacuum is good, the vapour particles travel in straight lines unimpeded by collision with residual gas molecules until condensed on a solid surface. A substantially uniform deposit is built up over the greater part of the specimen support-film, but sharply defined shadow regions behind each particle receive no metal and the lengths of these shadows, together with a knowledge of the shadowing angle, give the heights of the particles. Photomicrographs of such specimens, when printed with the shadows dark, give an illusion of oblique lighting.

(d) *Particle Size Analysis.* More especially in the field of industrial applications, numerical data on size and size-distribution of particles are often required and a brief discussion of this aspect of the subject is appropriate here. Particle-size in microscopy is usually taken to mean the diameter of a circle having the same area as the projected image of the particle, and sizing is usually carried out by comparison with calibrated circles on some form of graticule, for instance, those described by G. L. Fairs¹. In electron microscopy this can be done either on printed or projected images of the plates, and with practice, adequate precision in matching irregular areas can be achieved^{2, 3, 4}.

In the preparation of photomicrographs for such a determination, great care is needed in order to obtain thoroughly representative sampling. The aim is to produce specimens of sufficiently good dispersion to permit a perfectly random choice of fields. The number of particles required to obtain a sufficiently accurate result will vary with the spread of particle-size, but even at best the process is both lengthy and tedious.

Some progress has been made in recent years in the automatic sizing of particles, mostly in conjunction with the light microscope; some work has also been done on development of apparatus for automatic scanning of high contrast plates, such as may be produced in the electron microscope. These electronic methods measure the mean chords of the particles rather than diameters of equivalent circles⁵.

¹ *Journ. Roy. Micro. Soc.*, **71**, 1951, p. 209.

² W. H. Walton, *Trans. Inst. Chem. Eng.*, 1947, p. 51.

³ J. H. L. Watson, *Anal. Chem.*, **20**, 1948, p. 576.

⁴ L. le Bouffant and J. L. Soule, *Comptes Rendus*, **235**, 1952, p. 1207.

⁵ G. Haegermann, *Zement*, **31**, 1942, p. 441.

Results of a count may be treated in a number of ways in order to arrive at an average particle-size figure. In some cases the arithmetic mean is most useful; in others, the geometric or harmonic mean is more appropriate. The weighting of the various sizes recorded in counting may be assessed by a straightforward number or by a number multiplied by the first, second or third power of the projected area. These alternatives lead to the number, length, surface and volume- or weight-average particle-sizes. The most appropriate average to consider will depend on the application.

In the simple case of spherical particles, total surface area (A) of particles counted is:

$$A = \pi \sum d_i^2 n_i$$

where there are n_i particles of diameter d_i etc., the surface average particle-size is given by:

$$d_s = \frac{\sum d_i^3 n_i}{\sum d_i^2 n_i} \quad \text{(this is sometimes known as the volume surface mean particle size).}$$

Still considering spherical particles, the total volume of particles counted is given by:

$$= \frac{\pi}{6} \sum d_i^3 n_i$$

and the volume average particle-size is given by:

$$d_v = \frac{\sum d_i^4 n_i}{\sum d_i^3 n_i}$$

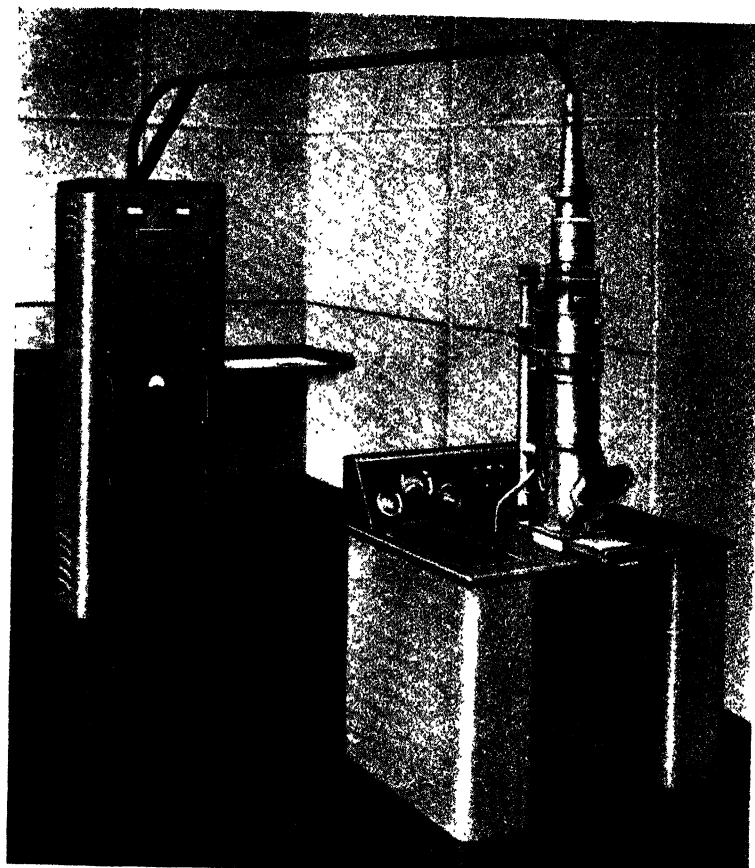
From the expressions for A and V it is seen that:

$$\frac{1}{d_s} = \frac{A}{6V} = \frac{\rho}{6} \frac{A}{\rho V} = \frac{\rho}{6} \times \text{specific surface area,}$$

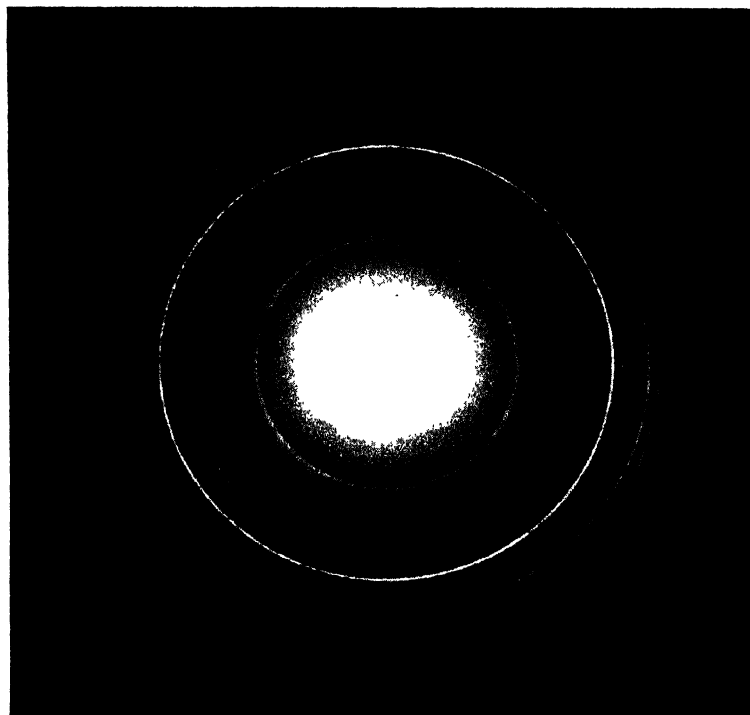
where ρ = density of the particles.

Thus in the case of spherical particles, the specific surface area is related to the surface average particle size by a factor of $6/\rho$. This factor also holds for cubic particles, but for all other shapes it is higher. It is found to be roughly constant for materials from any given source and independent of size.

In many cases of industrial use of powders, *e.g.* where they are to be subjected to chemical processing or where packing of particles is concerned, the size-range is important; in addition to average size, a measure of the spread is required. In some instances where size-distribution approximates to Gaussian this can be done concisely by quoting the standard deviation. Distributions are, however, often broad and asymmetrical, not characterized by such a single



METROPOLITAN-VICKERS EM3A ELECTRON MICROSCOPE.
(*Courtesy Metropolitan-Vickers, Manchester 17.*)



DIFFRACTION PATTERN OF KAOLINITE.

parameter. Further information will be found in Ch. XVI, while for a comprehensive account of small particle statistics the reader is referred to G. Herdan¹.

(e) *Surface Replicas*. Investigation of solid surfaces is for the most part carried out by examination of thin 'replicas' of such surfaces. These replicas must be thin enough to transmit electrons fairly freely and must carry the contour detail of the original. They may be grouped into broad classes:

NEGATIVE REPLICAS. These may be made in Formvar or collodion by flowing a dilute solution (about 0.25%) of the material over the surface to be replicated. When the coating has dried it is floated off on to a water surface, perhaps with the aid of a needle to tease it loose, where it is transferred to specimen grids. Fig. 81 represents such a replica before

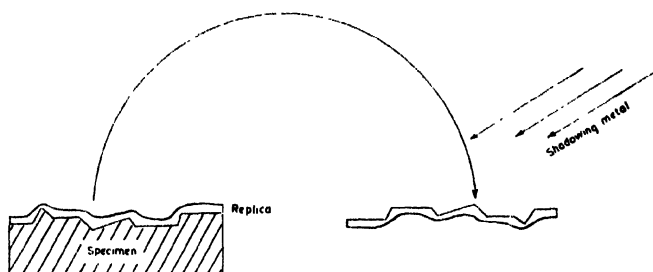


FIG. 81. Shadowed Negative Replica.

separation from the sample. Detail is rendered visible in the microscope as variations in thickness presented to the electron beam. The upper surface will not be flat nor will a perfectly uniform layer be formed, following surface detail. There will obviously be a tendency for corners to be filled in and interpretation of electronmicrographs from such replicas may sometimes be difficult. Metal shadowing, as previously described in discussion of power samples, may be applied with advantage to the underside. Detail then seen relates more strictly to sample surface detail.

POSITIVE REPLICAS. These are essentially a two-step process involving first the production of a thick negative replica of the surface under examination. The surface of this negative impression, formed in contact with the sample, is then in turn used for production of a replica which should faithfully reproduce the shape of the original surface.

This method is useful with rougher surfaces where a fragile negative replica has not the mechanical strength to permit stripping. It also facilitates the use of replica materials which must not be brought into contact with the original surface or which cannot be stripped from it.

¹ *Small Particle Statistics*, (Elsevier, Amsterdam), 1953.

One such method consists of the production of a thick polystyrene negative and from this a silica or silicon monoxide positive. The former is made either by flowing on a layer of lacquer or by pressing the sample and a block of the plastic together at elevated temperature. The thin positive replica is made by vertical deposition from the vapour phase under high vacuum and is separated from the polystyrene by solution of the latter. These replicas are strong and very resistant to heat in the microscope, but they are difficult to see and to handle. (See comments on silica and silicon monoxide substrates, p. 508).

A more satisfactory method of this type is based on carbon films¹. The thick negative replica is made in Formvar using a 0.25% solution and is reinforced for stripping with a backing layer of another plastic. The carbon positive replica is formed on the Formvar negative impression, by deposition from the vapour phase. These replicas are readily visible by reason of their brown colour; they are also easy to handle.

Other materials employed for the thin positive are a plastic soluble in a liquid which does not dissolve the negative replica, or the metals aluminium and beryllium^{2, 3, 4} or silica⁵ and silicon monoxide⁶. As with negative replicas previously described, results are much enhanced by the use of heavy metal shadowing.

PSEUDO-REPLICAS. If a thin layer of a plastic is cast on the surface of a solid built up of particles not adhering strongly together, then sometimes on stripping the film, the outermost layer of particles is also removed. Such specimens have been termed pseudo-replicas. On examination in the electron microscope they give information on the individual particles and the way in which they build up the solid.

OPERATIONAL TECHNIQUES

(a) *Adjustments and Precautions.* As in optical microscopy, it is necessary for good results to observe a number of precautions and to ensure that the instrument is properly aligned and adjusted. Brief reference is here made to essential points; for fuller treatment the reader is referred to standard works on electron microscopy (see bibliography, p. 521).

The electron beam is very sensitive to stray magnetic fields so that it is essential not to have any electrical equipment producing large stray fields nearby; in this connexion, it is common practice to install the high-voltage generator of the microscope in a separate cabinet suitably remote from the instrument itself.

A blurred image ('unsharpness') may also result from mechanical vibration. This is becoming less of a problem with the short sturdy

¹ D. E. Bradley, *loc. cit.*

² F. E. Carpenter and J. A. Curcio, *loc. cit.*

³ N. Hast, *loc. cit.*

⁴ W. Kaye, *loc. cit.*

⁵ C. H. Gerould, *loc. cit.*

⁶ G. Haas, *loc. cit.*

columns of modern instruments, but occasionally, perhaps when a specimen-holder is not seating properly, acute sensitivity to mechanical vibration is observed. It is always wise to minimize mechanical disturbances when exposing plates.

If the best performance of the microscope is to be realized, it is necessary to have it accurately aligned. It is impossible to define detailed procedure in the space available here, but the aim generally is to use the various traversing and tilt motions provided, so that a symmetrical, suitably intense electron beam is directed through the instrument to pass axially through the centres of all the lenses. The motions provided vary from one design to another, hence also recommended procedures. In checking alignment, use is made of the image-rotation produced by a magnetic electron lens. When alignment is correct, small variations of either lens-power or electron accelerating potential will be seen to cause a rotation and change of image-size, but no general lateral motion. Alignment carried out and checked by lens-current variation is referred to as current centering. Where the voltage is altered, the operation is referred to as voltage centering. With most instruments the two centres agree very closely. Correct alignment is so critical an adjustment that with many instruments it is not usually retained for any length of time and checking is periodically necessary during operation.

Other causes of poor results are dirt in vulnerable parts of the microscope, *e.g.* lens pole-pieces, where it may charge up and interfere with imagery; also specimen-drift due to thermal expansion on absorption of energy from the electron beam; this latter is minimized by allowing a short time to elapse after final adjustments and before exposing plates.

(b) *Electron Micro-Diffraction.* According to the Abbe theory of spectra in the light microscope, the periodic nature of the structure of crystalline material gives rise to sets of parallel diffracted rays (electron paths) in the electron microscope which, on passing through the objective lens, are brought to focus in the back focal plane of that lens. Thus, when a suitable specimen of crystalline material is being examined, there exists in this back focal plane a diffraction pattern characteristic of the sample substance. This pattern may be made visible on the fluorescent screen by reducing the power of the intermediate lens, so that it focuses the back focal plane of the objective and not the image produced by that lens. With this adjustment the projector-lens produces an enlarged diffraction pattern on the screen (see Pl. 23). For polycrystalline samples the pattern is a set of concentric circles; from the diameters of these circles it is possible to calculate the spacing of the Bragg planes¹, the structural

¹ See Ch. XIII.

periodicity responsible for each. These spacings and corresponding intensities of diffraction are characteristic of the sample material and may be used for identification purposes by reference to a card index system compiled by the American Society for Testing Materials¹. This index is based mainly on published x-ray diffraction data, but it is equally applicable to electron diffraction. It contains the diffraction of patterns of about 5000 substances, including a large number of minerals. These patterns are filed in numerical order of the 'spacings' of their three strongest diffractions. In dealing with an unknown substance therefore, the spacings of its three strongest diffractions are measured and a search is made for a card or cards with these strongest diffractions. Detailed comparison of likely cards with the data of the unknown may then lead to identification.

With electron diffraction there are many more obstacles to successful identification than there are in x-ray analysis. The thin layers of material giving rise to electron diffraction patterns are prone to change composition in the microscope. The high vacuum and heating effect of the electron beam may dehydrate the specimen or give rise to a metaphase. For well-formed crystallites, there is a tendency for preferred orientation to occur during specimen preparation; this is particularly bad with plates which tend to lie flat on the supporting membrane. If orientation does occur, relative intensities of the various diffractions are upset; some may even be absent which can be misleading. To the credit of the method, it can work with extremely minute quantities of materials, far less than would suffice for any other analytical method. It is possible to scan a microscope specimen in the usual way, then to diffract from selected small areas of that specimen.

APPLICATIONS

(i) *Natural mineral particles.* The electron microscope has greatly clarified ideas on finely-divided minerals, but it has not so far been widely applied to diagnostic work. This is no doubt due partly to the fact that it is insensitive to colour and refractive index, properties of considerable value in diagnosis. These disadvantages are to some extent offset by the possibility of obtaining diffraction patterns where sufficient sample penetration is possible, *i.e.* where particles are either very small or plate-like and suitably thin.

¹ *Alphabetical and Grouped Numerical Index of X-ray Diffraction Data*, A.S.T.M. Special Tech. Publ. No. 48-B (American Society for Testing Materials, Philadelphia), 1950. See also: J. W. Hughes, I. E. Lewis and A. J. C. Wilson, *Errors in the A.S.T.M. Index of X-ray Powder Diffraction Patterns*, (University College, Cardiff), 1956.

M. von Ardenne and V. Hofmann¹ found characteristic differences between bentonites from Wyoming, Geisenheim, California and Ponza. They also examined soils from Brazil and Java composed of fine particles of iron oxide and hydrargillite, and montmorillonite, respectively.

V. Hofmann, A. Jacob and H. Loofmann² used the electron microscope in conjunction with x-ray diffraction and established the differences of crystal habits of montmorillonite, saropatakite and kaolinite present. They were also able to recognise grains of quartz and Fe_2O_3 .

L. T. Alexander and others³, using the electron microscope in the course of x-ray work on clay minerals, reported endellite and halloysite to have lath-like crystals and confirmed the hexagonal plate habit of kaolinite.

R. P. Humbert⁴ published electron micrographs of montmorillonite, nontronite, illite, beidellite, hectorite, kaolinite, dickite, halloysite and of three clays, Sciotoville fireclay, ball clay and attapulgite. That author also noted variations in montmorillonite structures and a tendency towards fibrous structure in clays containing MgO ; he found mineral impurities clearly evident in the clays and concluded that the electron microscope might offer a means for rapid selection of raw materials for certain purposes.

T. F. Bates and others⁵ showed from electron photomicrographs that chrysotile crystals are hollow cylindrical tubes with a strong resemblance to crystals of endellite. W. Noll and H. Kircher⁶ confirmed these findings and also published data on amphibole asbestos and antigorite.

P. G. Nakin⁷, in a study of Californian oil-bearing formations, assessed the value of a number of analytical methods in the identification of clays. The methods he used were: x-ray diffraction, electron microscopy, thin section petrography, infra-red spectroscopy and cation exchange analysis. He concluded that no one method was diagnostic for all of the clay minerals.

O. E. Radczewski⁸, working on soils containing montmorillonite, nontronite, mica, kaolinite and diaspore, found that when x-rays did not give dependable results, the electron microscope could often identify the minerals, particularly when used in conjunction with electron diffraction.

More recently J. Wiegmann⁹, in a paper on electron optical examination of clays, discussed identification of kaolinite, montmorillonite and halloysite and stated that impurities are easily detected even in the finest fractions. Discussion of specific impurities is included.

¹ *Ber. Dtsch. Keram. Ges.*, **21**, 1940, p. 209.

² *Bodenkunde u. Pflanzenernähr.*, **25**, 1941, p. 257.

³ *Amer. Mineral.*, **28**, 1943, p. 1.

⁴ *Bull. Amer. Ceram. Soc.*, **21**, 1942, p. 260.

⁵ *Science*, **111**, 1950, p. 521.

⁶ *Neues Jahrb. Mineral Monatsh.*, 1951, p. 219.

⁷ *Journ. Petroleum Tech.*, **3**, 1951, p. 151.

⁸ *Z. Pflanzenernähr Düng. u. Bodenk.*, **57**, 1952, p. 66.

⁹ *Silikattech.*, **4**, 1953, p. 546.

(ii) *Industrial*. In this field a considerable effort has centred in cement and ceramics. In these particular applications, German workers have been prominent using microscopes equipped for observations at elevated specimen temperatures.

W. Eitel found the electron microscope to be a useful tool for studying solid state reactions and recrystallization phenomena in cement manufacture and he has contributed a number of papers on the subject^{1, 2, 3, 4, 5, 6}. With associates, he also studied hydration processes in lime, tricalcium silicate and tricalcium aluminate^{7, 8, 9, 10, 11}.

M. von Ardenne and K. Endell¹² made observations on melting of clinker minerals and Portland cement clinker at temperatures up to 1600°C. C. M. Sliepcevic and others¹³ made a study of crystals from the hydration of Portland cement.

M. von Ardenne and others^{14, 15} investigated sintering and melting, at temperatures up to 1600°C, of a number of minerals including magnesite, dolomite, feldspar, Pelssen clay, micaceous clay, a calcium bentonite and various kaolins. The effect of feldspar impurities on sintering of kaolin was also studied. Changes in clay minerals on heating were also investigated by W. Eitel¹⁶, who made observations on kaolin, montmorillonite, halloysite, talc and soapstone.

Considerable use is made of fine mineral particles as pigments and fillers for paints, rubber and plastics. In the case of white pigments, the most efficient particle size (for maximum hiding power) is about $\frac{1}{2}\mu$ and with tinting pigments, particle size can usefully be very much smaller. Here, therefore, the electron microscope is a vital tool for investigation of particle size and shape^{17, 18, 19, 20, 21}.

In the case of fillers, incorporated to modify rheological or mechanical properties of the products, particle-size tends to be somewhat

¹ *Naturwiss.*, 27, 1939, p. 807.

² *Zement*, 28, 1940, p. 693.

³ *Übermikroskopische Forschungsmethoden*, (W. de Grueter), 1941, p. 48.

⁴ *Z. Angew., Chem.*, 54, 1941, p. 185.

⁵ *Zement*, 31, 1942, p. 505.

⁶ *Ber. Dtsch. Keram. Ges.*, 24, 1943, p. 37.

⁷ E. Radczewski, H. O. Mueller and W. Eitel, *Zement*, 23, 1939, p. 1.

⁸ *ibid.*, p. 693.

⁹ *idem.*, *Zement*, 28, 1939, p. 693.

¹⁰ *idem.*, *Naturwiss.*, 27, 1939, p. 807.

¹¹ *ibid.*, p. 837.

¹² *Giesserei*, 30, 1943, p. 6.

¹³ *Ind. Eng. Chem. (Ind. Ed.)*, 35, 1943, p. 1176.

¹⁴ *Ber. Dtsch. Keram. Ges.*, 24, 1943, p. 73.

¹⁵ K. Endell and M. von Ardenne, *Kolloid Z.*, 104, 1943, p. 223.

¹⁶ *Ber. Dtsch. Keram. Ges.*, 24, 1943, p. 37.

¹⁷ P. C. Carman and P. le R. Malherbe, *Journ. Appl. Chem.*, 1, 1951, p. 105.

¹⁸ H. S. Davidson, *Off. Dig. Fed. Paint Varnish Product. Clubs*, 309, 1950, p. 753.

¹⁹ F. Endter, *Farbe u. Lack.*, 57, 1900, p. 461.

²⁰ M. L. Fuller *et al.*, *loc. cit.*

²¹ H. C. O'Brian, *loc. cit.*

larger, but the size-distribution usually results in the presence of particles too small for light microscopy, so that here too the electron microscope is necessary for a reliable examination.

Electron microscopy has been of considerable help in the study of dusts, particularly in connexion with health hazards arising from mineral dusts in mines and factories. It is generally agreed that particle-size is an important factor influencing damage to the lungs caused by inhaled dusts, and a large proportion of the particles in airborne dusts are too small to be resolved by light microscopy. J. W. Sharpe and R. F. Hounam¹, for instance, showed that in coal dusts about 70% of the particles revealed by electron microscopy were less than 0.2μ in diameter. Silica dust, responsible for silicosis, contains large numbers of particles of the order 50\AA . Harmful asbestos dusts contain many particles nearly as small².

(iii) *Solid surfaces.* Replica methods of electron microscopy have been used in the study of mineral surfaces, but up to the present, applications have not been numerous.

N. Hast³ applied a modification of the pseudo-replica technique to a study of freshly fractured clay surfaces. Actually he used a thick layer of collodion which, on removal from the surface, pulled off a layer of the clay particles. These were given a thin evaporated layer of aluminium and the collodion was then removed by solution leaving the particles adhering to the metal layer. Specimens of this type showed kaolinite and montmorillonite to have rather similar structures, consisting of plates stacked in piles. The montmorillonite particles were believed to be about 120\AA across by, perhaps, 15\AA in thickness.

S. Iwao *et al.*⁴ used a plastic replica technique to examine silica rocks for micropores with fluid inclusions. They found characteristic differences with coarse grained vein-quartz, chalcedonic sinter and chalcedonic vein-quartz. They also concluded that the description of the silica rocks depends greatly on size of the micropores and their density of distribution. Further applications of electron microscopy of solid surfaces to petrographic problems are suggested.

On examination of polished mineral surfaces, J. Kenyon⁵ has shown structures not revealed by the optical microscope and has confirmed that ex-solution products can exist in mineral specimens down to very small particle-size. Particles of gold in cobaltite, laths of cubanite in chalcopryrite and lamellae of ilmenite in magnetite, were revealed.

In the field of industrial applications, P. P. Budnikov and V. S. Fadeeva⁶ have used negative collodion replicas to study a glazed mul-

¹ *Proc. Delft Conference on Electron Microscopy*, 1949, p. 186.

² J. Kühn, *Arch. Gewerbepath. Gewerbehyg.*, **10**, 1941, p. 473.

³ *Nature*, **159**, 1947, p. 354.

⁴ *Japan Assoc. Mining Petrol. Econ. Geol.*, **37**, 1953, p. 167.

⁵ *Nature*, **172**, 1953, p. 114.

⁶ *Ogneupory*, **17**, 1952, p. 228.

lite body; T. Tanaka and N. Rynicki¹ have studied etched sections of cement-clinker (the kiln product before grinding), and A. Swineford and N. Plummer² have made an examination of fired glaze surfaces.

FUTURE TRENDS

As electron microscopes steadily increase in number, more petrologists will be able to make use of them. The type of instrument probably to prove most attractive to petrologists is that providing moderate performance combined with relatively low cost, since for much of the work in petrography the ultimate in resolution is not required. Despite their lack of refinements however, instruments in this class already provide resolution limits of between 50Å and 100Å and further improvements may well occur. Undoubtedly too there will be an upward trend in reliability, and in simplicity and speed of operation, which should improve the economics of the use of such instruments.

Of additional facilities available, those allowing for micro-diffraction appear to offer most scope to the petrologist. As already indicated, technique is simple but interpretation of results may be difficult; further, it seems possible that one of the main obstacles to widespread use of this technique will be supply of sufficiently trained and experienced personnel; this problem may not be so acute in those laboratories already using x-ray diffraction.

Many instruments now offered have facilities for small angle reflection work. Owing to restriction to examination of electrically conducting surfaces only, this technique has not as yet been applied by petrologists. There are, however, two ways in which this difficulty may be, at least partially, surmounted. At moderate magnifications, it is possible to obtain, by vacuum evaporation, reflecting metal films which are thin enough not to obscure any significant detail and which enable the coated sample to be observed directly. An alternative is to prepare a normal metallic replica and to examine this by reflection. At first sight this procedure might seem to have no advantage over the preparation of a normal shadow cast replica and its examination by transmission; but the extreme foreshortening, which has been previously referred to as making certain difficulties in interpretation of reflection pictures, may in some cases be an advantage, by showing a much larger area of the surface at one time.

A field of possible development which may be of great value to petrologists, is that of scanning electron microscopes. Cosslett and Duncumb³ have described an experimental instrument in which a

¹ *Journ. Ceram. Japan*, **60**, 1953, p. 20.

² *State Geol. Surv. Kansas Bull.*, **102**, 1953, p. 117.

³ *Proc. Electron Microscopy Conference*, Stockholm, Sept. 1956, p. 12.

finely focused beam of electrons strikes a specimen at normal incidence and may be made to scan a small area. Either the scattered electrons, or the x-rays emitted by the sample, may be detected and used to provide a signal for modulating a cathode ray tube scanned in unison with the specimen. If the x-rays are picked up with a proportional counter and pulse height selection circuitry, preset for selected elements, then the cathode ray tube displays the distribution of that element in the sample. It is also possible to stop the scan at any point, and to examine the characteristic x-rays emitted by that sample point using an x-ray spectrometer attachment. In this way a point by point elemental analysis may be obtained.

Another field, in which further development is likely to occur, is that of automatic counting and sizing of small particles. As already indicated, instruments have been constructed for determination of size distributions of particles under the light microscope, or from micrographs. It would be a great advantage to be able to use the electron microscope directly, and thus to eliminate the photographic recording process. This will have to be done with a scanning type microscope, and if it is done with one such as that of Cosslett and Duncumb, a remarkably versatile instrument will result.

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CHAPTER XV

NUCLEAR METHODS IN MINERAL AND ROCK ANALYSIS

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Introduction—Radioactivity—Types of Radioactive Decay—Nuclear Fission—Radioactive Series—Radioactive Equilibrium—Detection and Measurement of Radiation—Geiger-Müller (G.M.) Counter—Scintillation Counter—Accessory Electronic Equipment—Portable Field Instruments—Use of Nuclear Methods in Search for Economically Important Ores and Minerals—Radiometric Prospecting—Sources of Error—Radiometric Surveys—Further Applications—Radiometric Assaying—Autoradiographic Techniques—Alpha-particle Autoradiography—Beta-particle Autoradiography—Quantitative Measurement of Radioactivity from Emulsions—Radioactivation Analysis—Application to Mineralogy—Application of Mass Spectrometry to Mineralogy—Mass Spectrometer—Isotope Dilution Technique—Recent Geological Applications of the Isotope Dilution Technique—Geochronology—Stable Isotope Abundances.

INTRODUCTION

IN contrast to methods of mineral and rock analyses described in Chapters VIII and IX, depending almost entirely on behaviour of electrons surrounding nuclei of individual atoms of which the mineral is composed, methods now dealt with owe their applicability to certain highly important and characteristic properties of nuclei of the atoms. The methods may be divided into two main groups; the first utilizes the fact that nuclei of many atoms are either naturally radioactive or can be rendered radioactive by artificial means; this is a phenomenon of great importance in search for economically valuable radioactive mineral deposits, as well as for localization of small amounts of highly radioactive minerals within a body of rock; also for study of distribution of minute

quantities of trace elements within many minerals by the recently developed radioactivation analysis technique. A number of well-established methods is now in existence for detection and quantitative measurement of radioactivity, largely resulting from constantly increasing interest and importance of nuclear sciences over the last few decades.

The second of the two groups of methods depends upon determination of masses of the isotopes which together constitute one particular chemical element. The mass spectrometer is used to measure the isotopic composition of the element quantitatively and is applied particularly in conjunction with the isotope dilution technique. A sensitive and accurate method of analysis is hereby made possible for many, not necessarily radioactive, trace elements. In addition, determination of the isotopic ratio and its variation in many naturally-occurring elements is of outstanding and fundamental importance in some geological problems, particularly those concerned with absolute measurement of geological time and with conditions and processes affecting a rock or mineral during and since the time of its formation. At the outset, reference should, if necessary, be made to standard works on Chemistry for information relating to atomic structure and its significance in relation to the theory underlying the methods dealt with in this chapter.

RADIOACTIVITY

A radioactive substance is one possessing an inherent atomic instability which periodically causes one of the atomic nuclei to undergo partial disruption. This occurs at random and it is impossible to predict the exact moment at which any given atom will decay. Nevertheless, by considering a sufficiently large number of atoms, a certain definite fraction will decay in unit time. This fraction, which is termed the decay constant λ and which is quite characteristic for any given radioactive species, is not affected by any known chemical or physical processes; it seems reasonable to assume that λ has remained constant throughout geological time.

The rate of radioactive decay follows an exponential law. This means that if we start with N_0 radioactive atoms at time $t = 0$, there will be $N = N_0 e^{-\lambda t}$ atoms at some later time t . There is thus only a probability of any particular atom disintegrating at any given moment and this is proportional to the total number of atoms present. Gradual decay is explained by the fact that the length of time a radioactive atom can exist before disintegration can have all possible values from zero to infinity, otherwise all atoms would decay at once. However, the *average* life period for an aggregate of many atoms can easily be shown to be $1/\lambda$.

The half-life T of a given radioactive element is defined as the length of time required for half of any given number of atoms and thus of any given amount of the material to decay. The relation between T and λ , the decay constant, is given by:

$$T = \frac{\log_e 2}{\lambda} = \frac{0.69}{\lambda}$$

Obviously T is also a characteristic constant for a particular radioactive isotope. In different isotopes it may range from a few microseconds to many hundreds of millions of years.

TYPES OF RADIOACTIVE DECAY

Alpha-particles. A number of isotopes of the naturally-occurring heavy elements, such as the uranium isotopes of masses 238 and 235 (^{238}U and ^{235}U) and of thorium, mass 232 (^{232}Th), decay by the emission of alpha-particles (α -particles). An alpha-particle is, in fact, identical with a positively doubly-charged helium atom. Obviously, in any alpha-decay, the original charge and mass of the parent nucleus are decreased by two positive units and four units of mass respectively, and the daughter nucleus belongs to an isotope of the element two places earlier in the Periodic Table.

A given alpha-emitter always emits alpha-particles with a definite energy value. This value is generally high, but since alpha-particles are highly charged, their penetrating power through matter is very low. The range of an alpha-particle depends on the type of medium being traversed and in an average mineral or rock is not greater than about 0.03 mm. The range in air is several centimetres.

Beta-Particles. A large number of naturally-occurring and artificially prepared radioactive isotopes decay by beta-emission (β -emission). A beta-particle is similar to an electron but originates from the atomic nucleus by conversion of a neutron into a proton. This leaves the mass of the new nucleus almost unchanged but increases the atomic number by unity. The resulting daughter nucleus thus belongs to an isotope of the element one place later in the Periodic Table. Beta-particles from a given emitter have energies distributed continuously from practically zero to a definite and characteristic maximum (beta spectrum). Even the most energetic beta-particles will not penetrate for more than a few millimetres through most rocks and minerals and the problem of self-absorption of beta-particles by layers of these materials may be of some considerable importance in geological investigations; it often has to be allowed for in quantitative work.

Gamma-Rays. Most nuclei which undergo radioactive decay, especially of the beta-type, lose further energy by emission of one

or more gamma-rays (γ -rays) per beta-particle. These are a form of electromagnetic radiation analogous to x-rays, although the latter arise from energy transitions within the extranuclear electron shells, whereas gamma-rays arise from the nucleus itself. Their wavelengths lie between 10^{-8} and 10^{-11} cm. and each radioactive nucleus emits gamma-rays of a definite and characteristic energy. Also, if a nucleus emits several gamma-rays in quick succession, *i.e.*, passes through several successive unstable states, each will have a characteristic energy. This type of behaviour is quite different from the continuous beta-spectrum described above.

When traversing matter, gamma-rays lose most of their energy by colliding with extranuclear electrons and removing these from their atoms. In other words, they produce ionization, by which they can be detected. The degree of penetration of gamma-rays through matter depends on the energy of the rays and density of the medium traversed; the denser the medium, the more efficient the absorption of the rays. Generally the range in rocks and minerals may vary from a few inches to several feet, while the range in air may amount to several hundred feet, a property important for radioactive surveys from aeroplanes (*cf.* p. 538).

NUCLEAR FISSION

In nuclear fission an atomic nucleus may split into two parts which are generally not quite equal in size and which, in fact, constitute nuclei of two elements near the centre of the Periodic Table. Nuclear fission may occur spontaneously or may be induced by bombardment with neutrons and can take place in such heavy isotopes as ^{238}U , ^{235}U and ^{232}Th . The process occurs only to a limited extent in nature but it has some interesting laboratory applications, as will be seen later. The fission fragments are generally highly radioactive and decay through numerous and complicated series, involving production of beta-particles, gamma-rays and neutrons.

RADIOACTIVE SERIES

All isotopes of the naturally-occurring elements with atomic number greater than 82 (lead), undergo spontaneous radioactive decay. Each of the isotopes ^{238}U , ^{235}U and ^{232}Th stands at the head of a long and complicated series of radioactive disintegrations, and these three 'decay series' terminate at ^{206}Pb , ^{207}Pb , and ^{208}Pb respectively, the lead isotopes of these mass numbers being completely stable against radioactive decay. In nature, therefore, lead is constantly being produced by break-up of heavy nuclei, although the overall rate of accumulation is very low. As an example the natural radioactive disintegration series of ^{238}U is briefly summarized in

Table 27, p. 527. The great variation in half-lives of individual members of a series is to be noted. It is important to realize that almost all the radioactive steps involving beta-decay are accompanied by production of gamma-rays.

In each series (^{238}U , ^{235}U and ^{232}Th), several of the individual members can undergo radioactive decay by two distinct methods; the quantitative relationship between them is known as the branching ratio. Thus, in the ^{238}U family, the member ^{214}Bi can decay by beta-emission to ^{214}Po or by alpha-emission to ^{210}Tl . The branching ratio between these two processes is 99.96%: 0.04%, being greatly in favour of beta-emission. The ^{214}Po then emits an alpha-particle to give ^{210}Pb , while the ^{210}Tl gives a beta-particle and also decays to ^{210}Pb .

RADIOACTIVE EQUILIBRIUM

In radioactive series in general, a state of radioactive equilibrium will be set up when the rate of formation of a daughter isotope from its parent is equal to the rate at which it is itself disintegrating. In other words, for each decaying parent atom, one of each of the intermediate daughter atoms also decays, on the average. Thus ^{226}Ra emits an alpha-particle and among its products are three other alpha-emitters (*cf.* Table 27), namely ^{222}Rn , ^{218}Po and ^{214}Pb , with which it comes rapidly into equilibrium. Hence, at equilibrium, the resultant rate of alpha-emission will be four times that of radium alone. This does *not* mean that there will be equal masses of these four alpha-emitters present. Actual amounts of the individual members coexisting at equilibrium are directly proportional to their own characteristic half-lives; this is simply another way of saying that, within each member of a radioactive series at equilibrium, the same number of atoms disintegrate in a given time. Obviously the time taken to reach equilibrium from a single parent element depends on the half-lives of the succeeding elements in the series. Thus, pure ^{238}U will be in equilibrium with all its decay products after about 10^6 years.

Naturally-occurring radioactive elements are usually at equilibrium with their daughter products, but many instances are known where this is not so. Since radioactive parent and daughter atoms are chemically different, they can be separated in nature by geological processes. The nature and degree of non-equilibrium in a given sample of a radioactive rock or mineral frequently provide a clue to the geological history of the sample and its recognition may be of great importance in prospecting and assaying work. Reference may be made at this point to a review by T. P. Kohman and N. Saito¹.

¹ Radioactivity in Geology and Cosmology, *Ann. Rev. Nucl. Science*, **4**, 1954, p. 401.

TABLE 27
THE URANIUM²³⁸ DISINTEGRATION SERIES

<i>Elements</i>	<i>Symbol, Mass No. and Radiation</i>	<i>Half-life Values</i>
Uranium	²³⁸ U	4.50 × 10 ⁹ years
	↓ alpha	
Thorium	²³⁴ Th	24.10 days
	↓ beta	
Protoactinium	²³⁴ Pa	1.18 minutes
	↓ beta	
Uranium	²³⁴ U	2.50 × 10 ⁵ years
	↓ alpha	
Thorium	²³⁰ Th	8.0 × 10 ⁴ years
	↓ alpha	
Radium	²²⁶ Ra	1,622 years
	↓ alpha	
Radon	²²² Rn	3.825 days
	↓ alpha	
Polonium	²¹⁸ Po	3.05 minutes
	↓ alpha	
Lead	²¹⁴ Pb	26.8 minutes
	↓ beta	
Bismuth	²¹⁴ Bi	19.7 minutes
	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> beta ↓ ²¹⁴Po </div> <div style="text-align: center;"> alpha ↓ ²¹⁰Tl </div> </div>	<div style="display: flex; justify-content: space-between;"> 99.96% 0.04% </div>
Polonium	²¹⁴ Po	1.6 × 10 ⁻⁴ seconds
Thallium	²¹⁰ Tl	1.32 minutes
	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> alpha ↓ ²¹⁰Pb </div> <div style="text-align: center;"> beta ↓ ²¹⁰Bi </div> </div>	
Lead	²¹⁰ Pb	20 years
	↓ beta	
Bismuth	²¹⁰ Bi	5.0 days
	↓ beta	
Polonium	²¹⁰ Po	138.4 days
	↓ alpha	
Lead	²⁰⁶ Pb	(Stable)

DETECTION AND MEASUREMENT OF RADIATION

Introduction. There are two principal methods for measurement of nuclear radiation. The first of these depends on the ionization produced in a gas and employs two electrodes of opposite polarity to collect the ions formed, while the change in the potential difference is measured in an external circuit. The second method employs the minute light scintillations produced in certain special crystals or 'phosphors' by the radiation.

There are many ways in which these simple procedures may be adapted for measurement of any particular type of radiation under different conditions and in widely varying environments. For the geologist in the field or in the laboratory, the most important tools

are the Geiger-Müller counter for detection of beta-particles and gamma-rays, and the scintillation counter which can be made sensitive to most types of nuclear radiation.

GEIGER-MÜLLER (G.M.) COUNTER

This is probably more generally used in radioactivity measurements than any other single instrument. A G.M. tube consists essentially of a sealed, cylindrical glass or metal envelope, through the centre

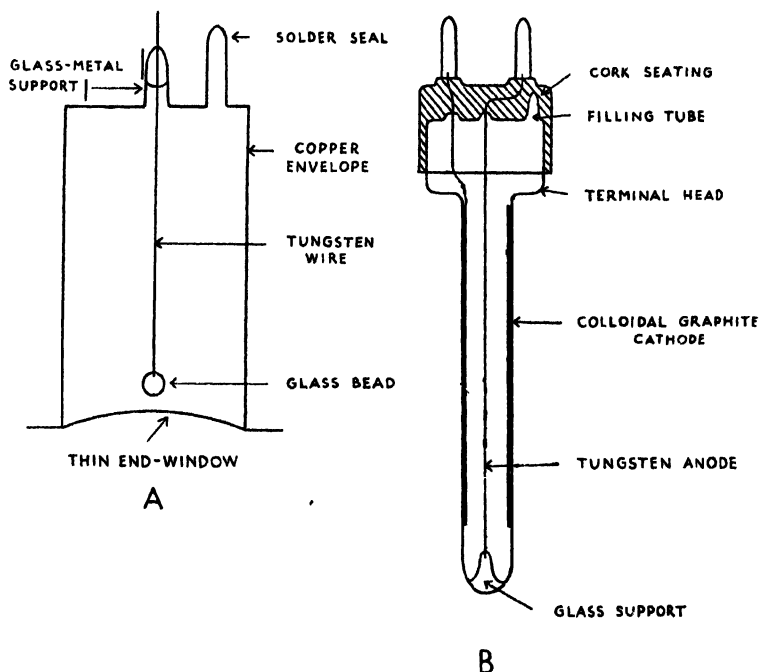


FIG. 82. Geiger-Müller Tubes.

A. For laboratory use.

B. Cylindrical thin-wall glass G.M. tube for field use.

of which runs a thin tungsten wire; during operation of the counter, the wire is kept at a steady potential between about 1,000–1,500 volts above that of the wall of the tube. The glass type has an inner concentric metal or graphite surface layer to act as low-voltage electrode. The majority of charged particles, *i.e.*, betas, entering the tube are attracted to the positively-charged central wire and on

arrival there produce an electric pulse which can then be amplified and measured. Each beta-particle in addition removes several extra nuclear electrons from the gas-atoms in the G.M. tube and these supplement the strength of the pulse generated by that particular beta-particle. Gamma-rays must produce a secondary electron by ionization to be counted, but the efficiency for this process is not greater than about 1%.

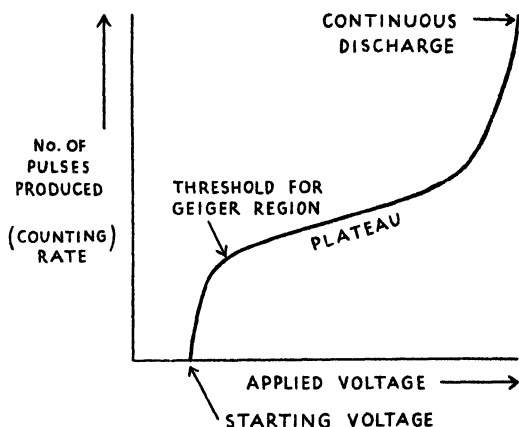


FIG. 83. Characteristic Curve of a Geiger Counter.

In many types of G.M. tube, especially those for field use, the entire wall is made of very thin glass or metal of about 0.0005 to 0.005 cm. thickness, so that most medium and high-energy beta-particles and all gamma-rays can enter the tube at any point on its surface. In the laboratory, however, it is more common practice for most investigations to use thicker-walled tubes with a very thin mica end-window where this may weigh as little as 1.5 mg./cm.² and through it beta-particles and gamma-rays of almost all energies can pass. In this case, the sample, in a small tray, is placed below the thin end-window before a measurement is made. Two typical G.M. tubes are shown in Fig. 82.

There are several other important features in G.M. counters. If a constant number of particles falls on the counter in unit time, then the number of pulses produced depends on the applied voltage in the manner shown in Fig. 83.

The actual voltage which is applied lies somewhere near the centre of the plateau and has to be individually determined before use for each G.M. tube. In this plateau region slight variations in the applied potential obviously have no serious effect on the number of pulses recorded.

In a counter, the pulse produced by a particle is, in the first instance, more like a continuous discharge due to the 'ion-avalanche' of secondary ionization electrons. It is of extreme importance that each discharge should be kept as short as possible and should be completely separated from the one that succeeds it. Only by doing this can the tube be used for counting a large number of particles or rays penetrating it in rapid succession. For this reason the tube is filled with gas at pressures ranging from a few centimetres to almost atmospheric. The most common mixture consists of argon with a small amount of an organic vapour such as alcohol or ethyl acetate. Such a mixture effectively quenches each discharge very quickly after its formation and after a very short rest period or 'dead-time' of about 10^{-4} seconds, the counter is ready for the next discharge. With this type of quenching, a G.M. tube can cope with counting rates up to a few thousand pulses per minute. Halogen quenched counters are now replacing the above tubes as they have many advantages including much lower operating voltage.

For counting alpha-particles the sample may be introduced into the counting volume of the tube itself with no intervening wall. The counter is then generally operated below the G.M. threshold-voltage in the so-called proportional region, where the magnitude of each pulse can be varied by changing the anode voltage. Such an arrangement is generally termed a proportional counter, but its geological applications are rather limited.

SCINTILLATION COUNTER

Although different forms of the scintillation counter can be used to detect and measure almost any type of nuclear radiation, from a geological point of view the instrument is used mainly for detection of gamma-rays in prospecting for radioactive materials. The rays produce tiny flecks of light or scintillations in certain crystals, such as thallium-activated sodium iodide. A small crystal is attached to the end of a light-sensitive photomultiplier tube and both are sealed up as a unit which must be completely impervious to light. From the photomultiplier the scintillations are transmitted as electrical pulses to an amplifier and then recorded.

The scintillation counter has a considerable advantage over the G.M. tube in that it is far more efficient for counting gamma-rays. Depending upon the type and size of crystal, scintillations may be produced by well over 50% of the coincident gamma-rays, whereas most G.M. tubes react to only about 1% of the gamma-rays which penetrate them. It can, therefore, detect much less radioactivity and at a greater distance from the source. Another advantage it possesses

is its shorter resolving time. The decay time of the phosphorescence in the crystal is approximately 2×10^{-7} seconds, whereas the 'dead-time' in a G.M. tube is of the order of 10^{-4} seconds. Consequently much higher counting rates are attainable. A typical scintillation counter tube is shown in Fig. 84.

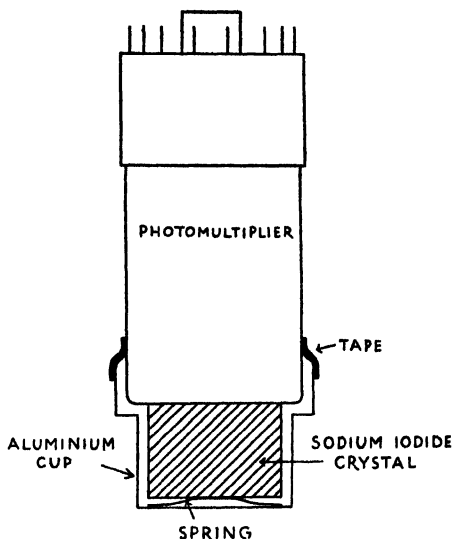


FIG. 84. Scintillation Counter for Gamma Counting.

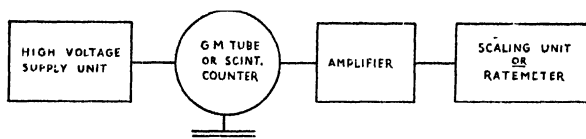


FIG. 85. Block Diagram of Typical Counting Assembly.

ACCESSORY ELECTRONIC EQUIPMENT

Detailed description of the great variety of modern electronic equipment used in radioactivity work can not be given here, but units in the block diagram (Fig. 85) in one form or another are essential for all work of this type.

The high-voltage supply unit supplies a stabilized high potential for the G.M. tube or for the scintillation counter photomultiplier tube. The amplifier magnifies the pulses received before transmitting

them to the scaler. In the latter, each pulse that arrives causes a small neon bulb to flash and provided the counting rate is not too high, each pulse is registered on a mechanical counter. Since the latter cannot function very rapidly, it is always necessary at medium or high counting rates to use the scaler with a factor of 10, 10^2 , 10^3 , or even 10^4 ; this simply means, say, in the case of the 10^2 scale, that for every 100 pulses arriving in the scaler, the mechanical counter ticks over only once. Obviously in this way, much greater counting rates can be mechanically recorded than would otherwise be possible. As an alternative to a scaler, it is not uncommon to use a ratemeter in which the individual pulses arriving from the amplifier are integrated into a direct current, which is then measured on an ammeter calibrated in pulses/second or pulses/minute. Ratemeters can be connected to automatic pen and ink recorders, thus giving a continuous automatic record of observations.

PORTABLE FIELD INSTRUMENTS

Geiger-Müller Units. Many compact, portable and reliable types of lightweight G.M. units are now commercially available for the individual prospector: see for example Pl. 24. There are, in addition, many different forms and sizes of tubes for special jobs such as car-prospecting, aerial survey, probing drill-holes, etc. For field work, the high-voltage power supply consists of dry batteries or accumulators (*i.e.*, car-batteries in mobile surveys). As above, the pulses are amplified and led into a scaler with neon-lights or into one which emits audible 'clicks' for each pulse received, or, alternatively, into a ratemeter. The G.M. tube itself is of the overall thin-walled type and in the case of individual prospecting equipment, is situated in a small, sturdy and easily handled probe unit, which the prospector carries in his hand.

Scintillation Units. Battery-operated types have only in recent years been made in small enough units for prospecting work. They are, as yet, somewhat more expensive than G.M. counters and not quite as sturdy, but nevertheless, owing to their greater sensitivity, they may eventually replace G.M. counters in the field to a considerable extent. At present G.M. tubes still have the advantage that they can be made quite easily in very large sizes, whereas it is more difficult to prepare large crystals for scintillation units. In general, portable scintillation counters are fitted with ratemeters and not with 'neon-light' or 'audible-click' scalers. Like Geiger-Müller tubes they are also used for car prospecting and in particular for radioactivity surveys from aeroplanes. For further details of atomic structure, radioactivity and methods of detecting and measuring

radiation, the reader is advised to consult the following references:

J. M. Cork, *Radioactivity and Nuclear Physics*, 2nd ed., (Van Nostrand, New York), 1950.

E. C. Pollard and W. L. Davidson, *Applied Nuclear Physics*, 2nd ed., (Chapman and Hall, London and Wiley, New York), 1951.

G. Friedlander and J. W. Kennedy, *Introduction to Radiochemistry*, (Chapman and Hall, London and Wiley, New York), 2nd ed., 1955. (Contains excellent introduction to the elements of Nuclear Physics.)

G. B. Cook and J. F. Duncan, *Modern Radiochemical Practice*, (Clarendon Press, Oxford), 1952.

USE OF NUCLEAR METHODS IN THE SEARCH FOR ECONOMICALLY IMPORTANT ORES AND MINERALS

As a result of the ever-increasing importance of atomic energy, there is given below a brief and simplified summary of some of the techniques and problems encountered in the application of the Geiger-Müller and scintillation counters in prospecting for uranium (to a lesser extent thorium, which is not yet of comparable importance); brief reference is also made to search for other important materials where a radioactivity survey can be of great assistance. This general topic is relevant here since an important part of the world's considerable uranium and thorium deposits occurs in sedimentary rocks, some covering vast areas. One of the best known of these regions, not yet fully explored due to its enormous extent, is the Colorado Plateau of North America, where many uranium ore-bodies occur in a thick succession of sandstones, shales and conglomerates, mainly of Mesozoic Age. A general description of this area has recently been given¹. A more detailed account by various authors on the wider occurrence and distribution of uranium and thorium in igneous and sedimentary rocks, ocean waters and sediments, etc., may be found in chapter 2 of the *Symposium on Nuclear Geology*, 1954², while a classification of uranium deposits according to host rock and origin has been made by D. L. Everhart³. The widespread and variable occurrence of uranium and, to a lesser extent of thorium, is due to its complex geochemistry; accounts of the latter are given by V. M. Goldschmidt⁴ and by K. Rankama and Th.G. Sahama⁵. A large amount of information on the geology and methods of prospecting for uranium and thorium has recently become available⁶.

¹ *Eng. and Mining Journ.*, Sept. 1954, pp. 87-117.

² H. Faul, *Nuclear Geology: A Symposium on Nuclear Phenomena in the Earth Sciences*, (Chapman and Hall, London and Wiley, New York), 1954.

³ *Origin and classification of Uranium deposits*, *Min. Eng.*, 6, 1954, p. 904.

⁴ *Geochemistry*, (Clarendon Press, Oxford), 1954.

⁵ *Geochemistry*, (University of Chicago Press), 1950.

⁶ *Proc. Inter. Conference on the Peaceful Uses of Atomic Energy*, Vol. 6: *Geology of Uranium and Thorium* (United Nations, New York), 1956.

RADIOMETRIC PROSPECTING

Field techniques for detection of uranium and thorium provide for beta- or gamma-radiation, since alpha-particles have too short a range to be readily detected in the field. Thus, most of the radiation comes not from the uranium and thorium themselves (these being alpha-emitters), but from some of the other elements in the uranium and thorium decay series, (*cf.* Table 27 and section below on equilibrium).

SOURCES OF ERROR

Background. There is some radioactivity everywhere and this 'background' activity is registered by every counter and must be checked frequently. It is contributed largely by cosmic rays, radioactive impurities in the counter itself and the usual trace amounts of radioactive material in the vicinity of the counter. The background count also varies from place to place and from time to time and this is due to variations in the cosmic ray contribution with altitude and topography, counter sensitivity, ageing of equipment, temperature changes, weak batteries and in particular by the different types of ordinary surface rocks containing varying trace amounts of the radioactive elements, uranium, thorium and potassium. (The naturally-occurring ^{40}K isotope is radioactive).

In general, radioactivity of light-coloured igneous rocks is greater than that of dark-coloured ones and of most sediments. Of the latter, black shales and phosphatic rocks are generally the most radioactive, limestones least, while sandstones vary a great deal. Thus, in traversing country from one rock-type to another, the background may alter considerably without there being any significant active ore-deposit. In all prospecting work it is always a significant increase in radioactivity above the general area background that is of diagnostic importance in the location of an ore-deposit.

Mass Effect. Unless this important effect is considered, the meaning of a measurement may be obscured. A counter does not measure the proportion or percentage of radioactivity in a rock or mineral, but rather the total amount of radioactivity that strikes it from the source. This is not to be confused with the counting efficiency of the instrument. Therefore the total radioactivity measured is not only dependent on the proportion and type of radioactive substance in the source, but also on the actual size of the source. A large piece of rock containing a certain percentage of radioactivity will give a larger reading than a small piece of the same rock; it is also important in comparing and interpreting readings, that the geometrical

relationship of the counter to, say, the rock-face under investigation, is the same each time, or that otherwise a correction factor is applied. Furthermore, if the counter is placed in a crevice or cave in the rock, a higher count is obtained since it is almost completely surrounded by the rock. In the same way, for a given rock-type, the reading obtained on a ridge may be only about one-half that obtained in a road-cutting. The mass effect becomes more apparant with increasing radioactivity of the rocks. Due to this effect it is essential to remember that a counter which has been calibrated against a standard sample of uranium or thorium cannot be used to estimate directly the grade of an outcrop or dump.

Absorption Effect. It is necessary to hold the counter at approximately the same distance from the source for strictly comparable readings, since otherwise variable absorption of the radiation in the intervening medium will occur.

It is also of importance to consider a buried radioactive source. The extent to which any substance absorbs gamma-radiation is roughly proportional to its density and solid rock has a considerable screening effect. It is found that one foot of inert igneous rock inserted between a uranium source and the detecting instrument will stop almost all the gamma-rays. The curves in Fig. 86 show the proportion of gamma-radiation from a large, deep source of uranium which would reach the surface through different thicknesses of inactive overburden of various densities. Consequently it becomes clear that without the use of drilling techniques, radioactive ore-bodies must be very near the surface of the ground to be detectable by surface or aerial prospecting. Aeroplane surveys are possible, of course, since the range of gamma-rays in air is several hundred feet, provided that the ore-body is very near the surface of the ground.

Equilibrium Effect. It was pointed out above that most radioactivity observed in the field comes not from alpha-emitting uranium and thorium but from their beta- and gamma-active daughter decay products. When an ore is in equilibrium (p. 526), a certain relative proportion of each daughter product is present, no matter what the grade of the ore; there is consequently a definite level of radiation for a given amount of uranium and/or thorium; it is only under these conditions that the amount of radioactivity (measured directly and dependent on the quantity of uranium and/or thorium present), is capable of providing a reliable indication of the grade of the ore.

Very frequently uranium minerals are not in equilibrium because they have been subjected to geological and chemical processes which have separated the uranium from its decay products and

insufficient time has elapsed for the restoration of equilibrium. Some uranium ore-bodies have been secondarily deposited from

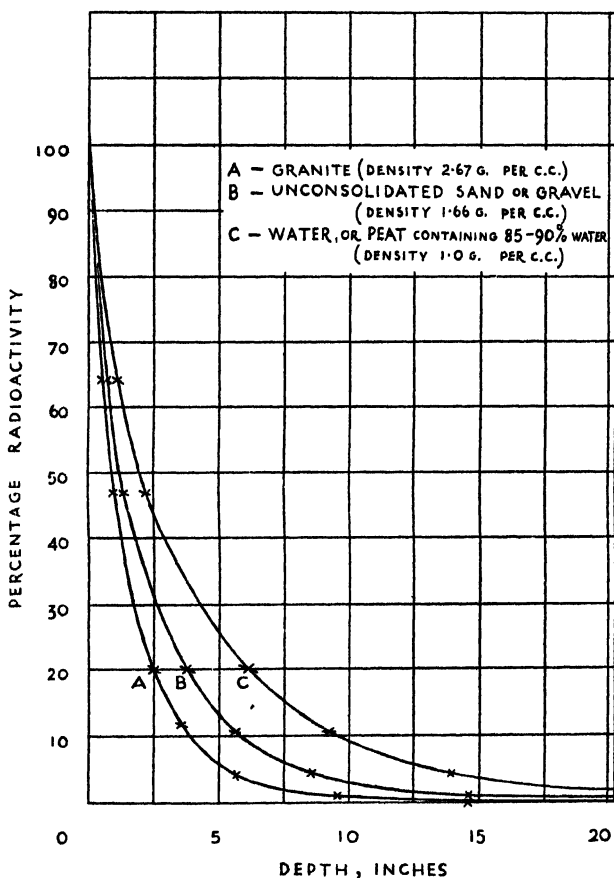


FIG. 86. Gamma-Ray Absorption Curves for Overburden Material of Different Densities.

(After S. H. U. Bowie, F. H. Hale, D. Ostle and K. E. Beer, *Radiometric Surveying with a Car-borne Counter*, 1955.)

circulating ground-waters and the daughter elements have not yet accumulated in their equilibrium amounts. In such cases there may actually be far more uranium present than is indicated by the counter reading. This is not so pronounced with thorium minerals, since these are not so readily weathered.

On the other hand, many primary uranium deposits, particularly those containing pitchblende (U_3O_8) with pyrite, chalcopyrite and chalcocite, undergo severe weathering, oxidation and solution due to formation of sulphuric acid from the sulphide minerals. The uranium is easily removed in acid solution, but some of the less-soluble daughter decay-products, such as radium and its associates, tend to remain behind in the weathered outcrop. Such sites may exhibit relatively intense radioactivity, despite the absence of uranium.

There is, unfortunately, no method for automatically correcting for lack of equilibrium in the field and therefore it is important to recognize conditions under which a counter reading may be reasonably reliable or otherwise. The following is taken from R. D. Nininger¹:

(a) *Generally Reliable*

- (i) Carnotite deposits of the Colorado Plateau type.
- (ii) Unweathered portions of pitchblende deposits.
- (iii) Unweathered portions of uranium-copper-sulphide deposits.
- (iv) Deposits of uranium in asphaltic sandstone.
- (v) Deposits of uranium in limestone.

(b) *Generally Unreliable*

- (i) Deposits of secondary uranium minerals in fractures or disseminated deposits of secondary minerals.
- (ii) Lacustrine deposits.
- (iii) Weathered portions of sulphide deposits.
- (iv) Radioactive coatings on mine-workings.
- (v) Encrustations around radioactive springs.

Underground Effect. Additional sources of error arise and must be taken into account when surveys are carried out underground in mines, old workings, etc.

- (a) The presence of radon in poorly-ventilated underground workings may give rise to a high background. The radon itself is not directly detected as it is an alpha-emitter; however, it decays comparatively rapidly and yields a beta- and gamma-active deposit (cf. Table 27).
- (b) The mass effect is extreme since the counter is entirely surrounded by rock. This tends to raise the background count considerably. Note, however, that the cosmic ray background is reduced with increasing depth, due to absorption in the overlying body of rock.
- (c) In wet mines, the tunnel-walls may be coated with a thin film of uranium salts deposited by ground-water. Since, however, they are probably of recent formation, they will not give very high readings.

¹ *Minerals for Atomic Energy*, (van Nostrand, New York), 1954.

RADIOMETRIC SURVEYS

It is outside the scope of the present chapter to describe in detail actual methods used in practice for radioactivity surveys. Suffice it to state that, if a general reconnaissance indicates an area of unusually radioactive rocks, it is then desirable to make a systematic radiometric 'grid' survey to determine the pattern of the radioactivity, to see whether it reveals valuable information for locating a commercial ore-deposit. The corrected readings are plotted on a map and contours are drawn connecting points of equal radioactivity (isorads). Such a map shows the size, shape and location of areas of highest radioactivity and will often provide a clue to an ore-belt or some mineralized structure otherwise not detectable.

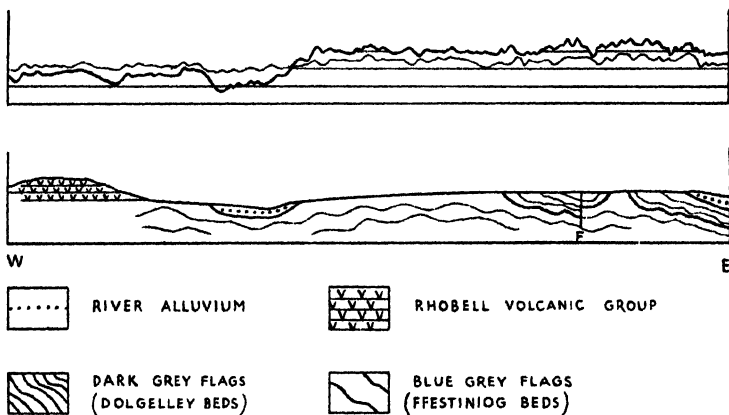


FIG. 87A. Car-Borne Radiometric Survey.
Radiometric profile and generalized geological section of a traverse
north of Dolgelley, Merioneth.
Thick line—Scintillometer trace; thin line—Geiger-Müller counter trace.

Briefly, reconnaissance radiometric surveys can either be carried out by individual prospectors on foot, carrying simple portable equipment or, as is common in the survey of larger unexplored areas, by car or aeroplane, fitted with counting and automatic recording equipment necessary for a continuous traverse. Numerous types of specially designed Geiger-Müller tube and scintillation counters are used for different kinds of work; during the past few years fairly standardized instrumentation and reconnaissance techniques have been developed for different methods of radioactive surveying.

Car-borne surveys are becoming increasingly important and have been used in many parts of the world. Several Geiger-Müller tubes or scintillation counters are connected to the usual electronic equipment

(powered by car battery) such as high-voltage supply, scaler, ratemeter and automatic recorder. At a constant and optimum speed of traverse, small pockets of mineralization, if sufficiently radioactive, will be indicated as a sharp peak on the recorder trace; whereas, a more widely disseminated occurrence will be recorded as a broader peak or plateau. Two typical recorder traces are reproduced in Figs. 87A and B.

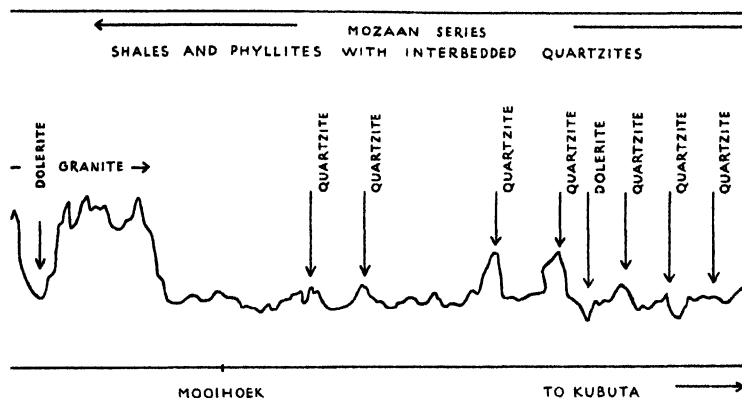


FIG. 87B. Radioactivity Profile of Karoo Dolerite, Maliduma Granite, and Mozaan Series.

(Figs. 92A and B after S. U. H. Bowie, F. H. Hale, D. Ostle and K. E. Beer, *Bull. Geol. Surv. Gt. Brit.*, 10, 1955, Fig. 7, p. 9 and Fig. 16, p. 21.)

It must be remembered that different types of rocks contain different trace amounts of radioactivity, so that care must be exercised in interpretation of results to prevent, for example, an ordinary rock with fairly high trace radioactivity being mistaken for an ore-deposit. A subsequent radiometric assay on specimens is, in any case, essential; see p. 541.

Variations in occurrence of natural radioactivity also make it possible frequently to use such surveys to detect the presence of formation contacts, shear and fault-zones and other structures, and to assist in mapping veins, dykes and igneous bodies differing in radioactivity from rocks surrounding them. Further details on radiometric prospecting and surveying are given in references below^{1, 2, 3, 4}.

¹ H. Faul, *ibid.*, p. 219.

² R. D. Nininger, *ibid.*, p. 163.

³ S. H. U. Bowie, F. N. Hale, D. Ostle and K. E. Beer, *Radiometric Surveying with a Car-Borne Counter*, *Bull. Geol. Survey Gt. Brit.*, No. 10, (1955), p. 1.

⁴ D. H. Peirson and E. Franklin, *Aerial Prospecting for Radioactive Minerals*, *Brit. Journ. Appl. Physics*, 2, 1951, p. 281.

FURTHER APPLICATIONS

Uranium ores may be sorted by using counters to detect comparatively highly radioactive lumps in conjunction with a suitable mechanical device for their separation from non-radioactive material. This process can also be extended to non-radioactive minerals (*cf.* section on radioactivation analysis, p. 547).

Geiger-Müller or scintillation counters can also be adapted to permit lowering the probe unit into a borehole and recording changes of radioactivity as it is moved vertically. Techniques of this borehole 'logging' are rapidly developing and are of great value in reducing the amount of core-drilling required in uranium exploration work. The object is to obtain a continuous record of gamma-activity plotted against the depth of the borehole. In accordance with principles previously outlined, a sensitive borehole counter can also be used in certain circumstances for distinguishing between different rock-formations penetrated, due to differences in degree of radioactivity, thus giving much useful geological information. Scintillation counters are sometimes used in oil-exploration, since oil-fields themselves tend to be low in radioactivity, but are often surrounded by a zone with somewhat greater radioactivity than normal.

Another technique of borehole logging, which may be used independently or in conjunction with the natural gamma-log method mentioned above, is based on the principle of neutron-activation (*cf.* p. 547). A source of neutrons, such as a radium-beryllium mixture, is lowered into the hole. Some of the elements in the rocks of the borehole slow down and capture the neutrons and emit gamma-rays, which are then detected and measured by suitable counting and recording equipment. The information is presented graphically as a neutron-gamma ($n\text{-}\gamma$) log. On the other hand the neutrons themselves may be detected after they have travelled some distance in the rock and have been slowed down. Depending on the degree of absorption by the rock, some return to the borehole where their presence is revealed by a neutron-detecting device. This method gives a neutron-neutron ($n\text{-}n$) log.

Hydrogen is the most effective element in slowing down neutrons and is also an important slow-neutron capturing element in many sedimentary rocks, due to reaction $\text{H}^1(n, \gamma)\text{H}^2$ (see p. 547). The ($n\text{-}n$) and ($n\text{-}\gamma$) log methods are very sensitive to presence of hydrogen, whatever its state of chemical combination within the traversed rock. For instance, rate of neutron capture, hence number of gamma-rays emitted, is greater in wet than in dry strata. Gamma-rays produced indirectly by the neutron source are generally stronger than any emitted from naturally radioactive elements present in the rock.

Since intensity of gamma-radiation produced on neutron-capture depends on the hydrogen content of the rock, neutron logs can be used to measure the amount of fluid such as water, brine, mud, natural gas, petroleum, surrounding the counter in strata or bore-hole. Neutron logs thus give a measure of porosity of a rock, since fluid occurs mainly in rock-pores. Neutron log methods in general can yield quantitative information of the hydrogen content of porous strata, while the (n-n) log can, in certain circumstances, be used to distinguish between fresh water and brine or oil occurring interstitially in sands, or between natural gas and oil or water.

In general, then, there is a tendency for different types of rock-formations to yield natural radioactivity and neutron logs of fairly characteristic size and shape. The logs are useful and important in petroleum geology, *e.g.* to distinguish between sandstone and shale, sandstone and limestone, etc., to measure thicknesses of rock-formations and to indicate presence of oil-producing sands. Due to high lateral persistence of some formations, the logs can frequently be used to correlate strata, as well as for sub-surface structural mapping, and in exploration for potash to distinguish anhydrous sylvite (KCl) from hydrated carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), the latter being less desirable as an ore of potash. Neutron and gamma-ray methods have also been developed for estimating moisture content and density of soils, as well as for many other types of bore-hole investigations. An excellent summary of gamma-ray and neutron logging in the petroleum industry and of nuclear logging of drill-holes for mineral exploration and soil studies, together with diagrams of typical apparatus and references to existing literature on the subject, is given in *Nuclear Geology*¹.

RADIOMETRIC ASSAYING

Counters for detection of nuclear radiation are used extensively in assay of minerals, ores and rocks for radioactive elements. Such assays can be made rapidly and accurately in the laboratory, somewhat less accurately in the field, by using portable equipment consisting of a hand-operated crusher, a counter, (generally a Geiger-Müller for beta and/or gamma counting), a portable scaler or ratemeter, a comparison standard, a watch and a suitable sample holder.

Without use of special absorbers, etc., a Geiger-Müller tube (or scintillation crystal) cannot distinguish between radiation from uranium, thorium, potassium, etc., so that an ordinary radiometric assay of a mineral or ore-specimen does not give actual sample composition. It is, therefore, general practice to assume a standard

¹ H. Faul, *ibid.*, p. 241.

composition of samples and to express all results in terms of that composition. Thus, assays can be expressed in terms of 'equivalent uranium' (eU), defined as the amount of uranium in equilibrium with its daughter elements required to give the same counting rate as the sample in the particular type of instrument used. One may define similarly equivalent thorium, equivalent potassium, etc.

It is desirable in assay work that the ore be in radioactive equilibrium. When there is a considerable and variable degree of disequilibrium in different samples, the best way is to determine uranium or thorium content by chemical analysis. The degree of disequilibrium can be determined if necessary by application of rather more complex radiochemical separation techniques¹.

In the assay itself, a known weight or volume of the sample is placed in a fixed geometrical relationship close to the counter, the counting rate determined and compared with the counting rate produced under identical conditions and with the same counter, by the same weight or volume of a standard sample of known composition, which must itself be in equilibrium. The background counting rate is also determined. The assay is given by the equation:

$$\frac{\text{Sample Assay}}{\text{Standard Assay}} = \frac{\text{Gross sample counting rate} - \text{background}}{\text{Gross standard counting rate} - \text{background}}$$

or from a graph prepared for that specific counter on a basis of measurements made on chemically assayed standard samples. For the purpose of routine beta-assaying of samples containing more than 0.0005 eU, shallow dishes filled level with the powdered sample are generally used with an end-window type Geiger-Müller tube, but other methods are also employed. Some form of lead or iron shielding around the tube is essential to cut down background counting rate.

Many radiometric assaying techniques have been described in the literature and for complete details the following references should be consulted:

F. L. Curtiss, Measurements of Radioactivity, *U.S. Nat. Bur. Standards, Circ.*, 476, 1949.

G. G. Eichholz, J. W. Hilborn and C. McMahon, The Determination of Uranium and Thorium in Ores, *Canadian Journ. Phys.*, 31, 1953, p. 613.

E. Franklin and R. K. Barnes, The Radiometric Assay of Uranium and Thorium Ores, (H. M. Stationery Office, London), *A.E.R.E. Rep.*, EL/R 1175, 1953.

G. G. Eichholz, Routine Radiometric Analysis for Uranium in Ores, *Canadian Dept. Mines and Technical Surveys, Radioactivity Division, Rep.*, TR-120/54, 1954.

¹ J. N. Rosholt, Quantitative Radiochemical Method for Determination of the Major Sources of Natural Radioactivity in Ores and Minerals, *Anal. Chem.*, 26, 1954, p. 1307.

So far techniques have been described which can be used either directly in the field or in small field laboratories such as may be found in ore-mills or assay offices. Such methods have been concerned almost entirely with search for new deposits of economic value and their evaluation. Several nuclear techniques will now be described which are of considerable significance in much recent research work; for these it is essential to have available resources and facilities which only a thoroughly modern and well-equipped laboratory can provide.

AUTORADIOGRAPHIC TECHNIQUES

Autoradiography depends upon the fact that photographic emulsions are affected by all types of nuclear radiation, of which alpha- and beta-particles are of particular interest to the geologist. J. Step and F. Becke (1904) were the first to use this technique for a study of distribution of radioactivity in specimens of the Joachimsthal pitchblende deposit, while O. Mugge (1909) found that other minerals, such as thorite, thorianite and allanite and several specimens of zircon, also blackened a photographic emulsion. This blackening is, in fact, due to a large aggregate of alpha-tracks, each of which is represented in the developed emulsion by a row of silver grains. Images produced by betas and gammas in a normal type of emulsion are rather more diffuse because of their far greater penetrating power; but in recent years numerous special, fine-grained emulsions, with high silver halide content, have been produced and may be used to record specifically alphas or betas, or both.

ALPHA-PARTICLE AUTORADIOGRAPHY

A polished section, plane-ground surface, or thin section of the rock or mineral is exposed in direct contact with the photographic emulsion, for a suitably long period and in complete darkness, with the eventual aim of superimposing and comparing the actual rock surface with the alpha-emission pattern obtained after the plate has been processed. Mineral grains from sands or silts can be similarly examined by embedding the grains in the moistened emulsion layer and distributing them as uniformly as possible over the plate. Average range of alpha-particles in the emulsion is generally about 20–25 μ .

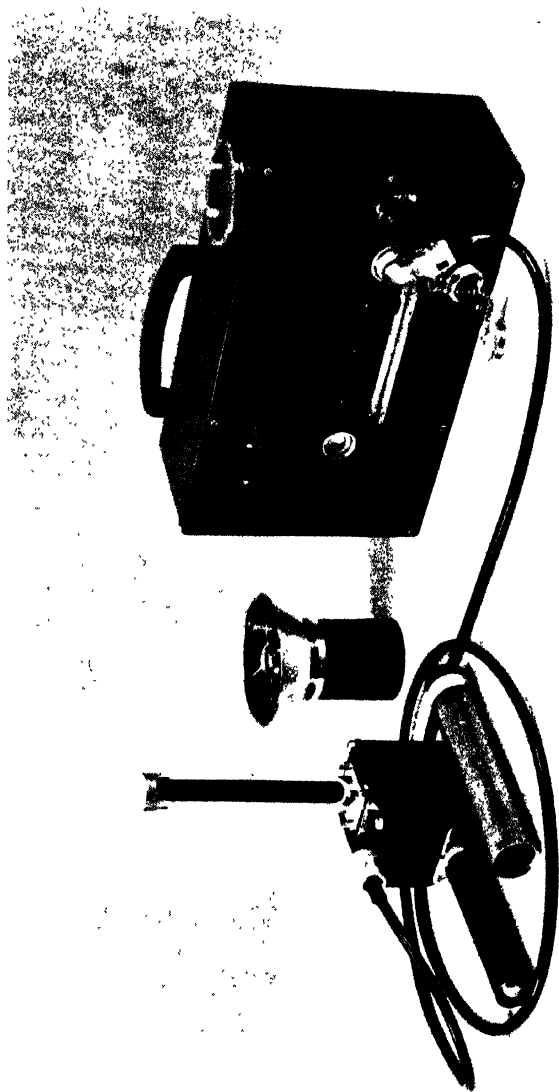
Alpha-particle autoradiographs are of great value for detection and precise localization of small amounts of radioactivity or radioactive minerals within a rock-specimen; also for a study of location and identification of uranium and thorium minerals in rocks consisting in part of non-radioactive minerals. It is thus a simple matter to distinguish between minerals with uranium and thorium as major

and minor constituents. They can also assist the geologist in deriving information concerning paragenesis of radioactive and associated constituents, as well as post-formational changes due to leaching, weathering, reprecipitation and metamictization, *i.e.* alteration due to radiation damage. Furthermore, the method is useful for studying radioactive homogeneity of a specimen before submitting it to chemical analysis or to radioactivity measurements, *e.g.* for purpose of absolute age determinations.

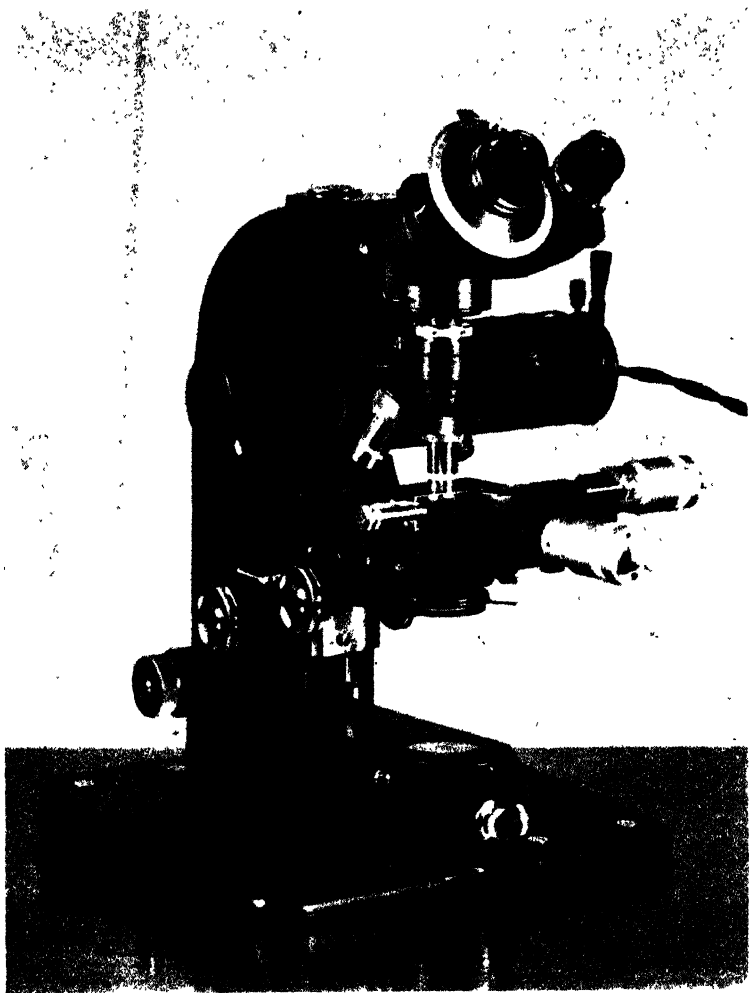
BETA-PARTICLE AUTORADIOGRAPHY

Emulsions sensitive to alpha- and beta-particles can be used for localization of uranium and thorium minerals as well as for distinguishing potassium-rich minerals emitting no alpha-particles by microscopic examination of the tracks. Beta-particle tracks tend to be thin and curved in contrast with thicker and straighter alpha-tracks and their image shows a poorer resolution than is the case with the latter. Beta-emulsions have also been found useful in neutron activation analysis of thin or polished sections. The principles of this type of analysis are more fully outlined on page 547. Suffice it to say that numerous ordinary, naturally occurring isotopes of elements, on bombardment by neutrons, form artificially radioactive isotopes readily detected and measured, serving to characterize and identify the original inactive isotopes. Thus a study of distribution of traces of manganese in certain ores has been made by subjecting a thin specimen of the ore to neutron bombardment, after which it was placed in contact with a nuclear emulsion. The ordinary, naturally-occurring manganese isotope ^{55}Mn , yields, by such treatment, the highly radioactive ^{56}Mn ; this decays by emission of beta-particles recorded by the emulsion. Other suitable elements whose trace distribution has been studied by this technique, are sodium, potassium, copper, arsenic, indium, barium, scandium, tungsten, gold and certain rare earths. It is fortunate that some common rock-forming elements, such as iron, sulphur, oxygen, aluminium and silicon, are not really as suitable for neutron-activation analysis as the elements mentioned above and in practice little, if any, interference is obtained from them. A semiquantitative assay of trace elements in the ore can be made if carried out in conjunction with measurements on known concentrations of the elements in question.

It is noteworthy that boron- and lithium-containing minerals can be localized and detected in trace amounts by neutron bombardment in contact with an alpha-emulsion, since in the case of these two elements, absorption of a neutron is followed by emission of an alpha-particle.



PORTABLE FIELD RATE-METER.
Courtesy Ericsson Telephones Ltd, London, W.C.2.



NUCLEAR RESEARCH MICROSCOPE.
(Courtesy Cooke, Troughton & Simms Ltd., York, England.)

A somewhat similar method has also been used by M. Debeauvais *et al.*¹ for localization of bismuth in minerals and rocks and its quantitative determination down to 10^{-8} g. Bi; this is better than any other analytical method for this particular element. It depends on absorption of a neutron by the naturally-occurring ^{209}Bi isotope to give ^{210}Bi ; β particle emission then yields ^{210}Po which emits an alpha particle; this can be used, by similar methods to those described below, for a quantitative estimate of the bismuth content of the original sample. References to much recent work of this type are given by K. Rankama² and by S. H. U. Bowie³.

QUANTITATIVE MEASUREMENT OF RADIOACTIVITY FROM EMULSIONS

Estimation from Image Density. As already mentioned, the overall macroscopic effect of numerous alpha-tracks obtained from a homogeneous and sufficiently strong radioactive source, such as uranium or thorium mineral placed in contact with an emulsion, is a blackening of the emulsion. This blackening is known as image density and it varies directly with alpha-activity of the material under investigation. The total uranium *plus* thorium present can be determined semi-quantitatively from the degree of blackening of the emulsion. This is measured by means of an electrical instrument known as a microdensitometer, using analysed standards for comparison. It is common practice to expose the standard and unknown side by side on the same plate and for the same length of time.

Estimation from Track Count. Alternatively, if the ore-mineral is of too low a grade to produce an image of suitable density for the densitometer, the particles given off during a given time interval may be determined by counting the number of alpha-tracks per unit area with the aid of a suitable travelling microscope fitted with a graduated eyepiece (see Pl. 25). The statistical error involved will, of course, depend on the number of tracks counted. In this way, the content of radioactive material, *e.g.* total uranium and thorium of the sample, may be determined, since the number of alpha-tracks in an emulsion in contact with the mineral is proportional to the content of the alpha-emitter in the sample and to time of contact.

It is also possible, though somewhat tedious, to determine indirectly the proportion of uranium to thorium when, as often

¹ M. Debeauvais, F. G. Houtermans, E. Jäger, W. Buser, *Tschermaks' Mineralogische und petrographische Mitteilungen*, Series 3, 5, No. 1-2, (1954), p. 129.

² *Isotope Geology*, (Pergamon Press, London), 1954, p. 121.

³ H. Faul, *ibid.*, p. 48 ff.

happens, they occur together. This involves counting tracks and measuring their lengths by means of the microscope. The method presupposes existence of radioactive equilibrium within the mineral since it is, in fact, necessary to count the alpha-tracks due to ^{212}Po and ^{214}Po occurring in the ^{232}Th and ^{238}U decay series, respectively. Each of these polonium isotopes emits an energetic alpha-particle of which, however, the known ranges within emulsion differ sufficiently to be used as a measure of uranium and thorium contents. It is therefore necessary to count the number of alpha-tracks possessing characteristic lengths of ^{212}Po and ^{214}Po alphas within the emulsion. The ^{212}Po alpha-particle has a range of 8.57 cm. in dry air at N.T.P.; the ^{214}Po under similar conditions has a range of 6.91 cm. Naturally these values are proportionally reduced by a factor of nearly 2,000 in a solid emulsion.

S. H. U. Bowie¹ suggests the following practical procedure to obviate counting and measuring a large number of alpha-tracks when determining respective uranium and thorium contents. A dual exposure of the section is made, first in direct contact with the emulsion and then with a thin layer of plastic between the emulsion and the specimen. He uses five layers each of 0.0005 in. Distrene, which together have a stopping power for alpha-particles equivalent to about 7.5 cm. of air and can thus discriminate satisfactorily between the two types of polonium alpha-particles. In addition, it is important to note when calculating results that the number of alpha-particles emitted per unit area of a thick uranium source in unit time is about 3.3 times that emitted by thorium under the same conditions.

Beta-emulsions have been used for quantitative measurement of potassium and rubidium in rocks and minerals. The beta radioactive isotopes of these two elements are ^{40}K and ^{87}Rb , of which a constant proportion is present in all naturally-occurring potassium and rubidium.

A great deal of work has been carried out in the last decade on characterization and quantitative determination of natural and artificial radioactive isotopes, using nuclear emulsion techniques, in particular by E. Picciotto and his associates in Belgium, in connexion with mineral and meteorite analyses, geological age determinations, deposition of ocean sediments, etc². Nevertheless, it should be pointed out that, in general, use of emulsions for assay of rocks by counting and measuring individual tracks, although invaluable to the specialist research worker, is in many cases too

¹ Autoradiographic Techniques in Geological Research, *Bull. Geol. Survey Gt. Britain*, 3, 1950, p. 58.

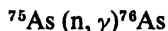
² E. Picciotto and S. Wilgain, Thorium Determination in Deep-Sea Sediments, *Nature*, 173, 1954, p. 632.

laborious and full of experimental defects and difficulties for routine application. For further details on autoradiographic technique, the reader is referred to S. H. U. Bowie¹ and H. Yagoda².

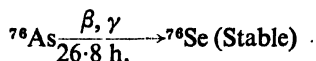
RADIOACTIVATION ANALYSIS

General Principles. With the advent of nuclear reactors and particle accelerators, there is now available an extremely sensitive and specific technique, involving a high degree of accuracy, for detection and determination of many elements, by forming their artificially radioactive isotopes, which can be identified and measured. Several types of nuclear particles and rays can be used to form such isotopes, but for present purposes slow neutrons are chiefly concerned, obtainable in large numbers from a nuclear reactor or, in smaller numbers, from a laboratory neutron source consisting of a mixture of a small amount of a radium and beryllium compound embedded in paraffin wax. The slow neutrons react with the element irradiated to yield in most cases an artificially-radioactive isotope of this element.

A typical example is the element arsenic, which consists in nature solely of the isotope ^{75}As . When natural arsenic is irradiated with slow neutrons, the nuclear reaction occurring can be written as follows:



this implies that a ^{75}As nucleus absorbs a neutron with formation of a ^{76}As nucleus and production of a gamma-ray. The ^{76}As nucleus is unstable and decays by beta- and gamma-emission into the stable selenium isotope ^{76}Se , with a half-life of 26.8 hours. This can be written:



The readily-measurable beta-gamma activity involved in this transition can provide a measure of the ^{76}As present, hence of the ^{75}As as well. The method obviously provides a measure of the total arsenic present in the original sample. Most (n, γ) reactions give rise to beta-gamma active isotopes which can be identified by their half-life and by characteristic energy of their radiation.

The intensity of radioactivity obtained, depends upon a number of factors:

- (i) Mass of the element or isotope irradiated.
- (ii) Slow-neutron intensity or 'neutron-flux' (expressed in neutrons/cm²/sec.) to which the sample is subjected. In the Harwell Pile, in

¹ H. Faul, *ibid.*, p. 48.

² *Radioactive Measurements with Nuclear Emulsions*, (Chapman and Hall, London and Wiley, New York), 1949.

which irradiation facilities are available on request, a flux of approximately 10^{12} neutrons/cm.²/sec. is available.

(iii) Length of time for which the sample is irradiated.

(iv) 'Effective nuclear area' that each atom of the element presents to the neutrons, *i.e.* its readiness to interact with them. This varies widely from element to element and isotope to isotope; it is called the 'activation cross-section' for the particular nuclear reaction in question. It has the units of cm.² and many cross-sections are of the order of 10^{-24} cm.², *i.e.* one "barn".

(v) Half-life of the artificially radioactive isotope produced.

(vi) Efficiency and sensitivity of the counting equipment used.

With all these quantities known, it is a simple matter to calculate sensitivity of the radioactivation method for a wide range of elements. The fundamental equation for radioactivation analysis is:

$$A = N \cdot f \cdot \sigma \cdot \theta \cdot (1 - e^{-\lambda t}) \quad \dots 1$$

where A = number of atoms disintegrating per second in the artificially radioactive isotope, or the 'Activity';

N = total number of atoms of particular element irradiated;

f = pile neutron flux;

θ = abundance of particular isotope giving rise to the activity;

σ = activation cross-section for relevant nuclear reaction;

λ = decay constant of artificially radioactive isotope. (Note that $\lambda = 0.69/T$ where T is half-life);

t = length of time of irradiation.

The above equation is more practically expressed in the form:

$$A = \frac{6.02 \times 10^{23} \times f \times \sigma \times \theta \times W(1 - e^{-\lambda t})}{M} \quad \dots 2$$

where W = weight of element activated; M is its atomic weight and 6.02×10^{23} is the Avogadro number.

Provided an irradiation time is assumed of several half-lives, which is quite feasible for many artificially radioactive isotopes, and considering only one microgram (10^{-6} g.) of the irradiated element, together with a flux of 10^{12} neutrons/cm.²/sec. available in the Harwell Pile, the last equation reduces to

$$A = \frac{3.6 \times 10^7 \times \sigma \times \theta}{M} \text{ disintegrations/minute,}$$

a useful simplification of the sensitivity formula for the element to be determined.

General Procedure. Consider a sample in which a small trace of copper is to be determined. For this purpose it must be irradiated at the same time and under exactly the same conditions as a standard sample with known copper content. The amount of radioactive copper produced in each is then measured, again under identical conditions, by standard counting techniques. The equipment for the

latter generally consists of an end-window Geiger-Müller tube, shielded well by lead, coupled to a power pack and a scaling unit. It then follows that:

$$\frac{\text{Sample Count}}{\text{Standard Count}} = \frac{\text{Mass of copper in sample}}{\text{Mass of copper in standard}}$$

In practice it is likely that the irradiated sample contained other elements besides copper and some of these may also become significantly radioactive. If the latter cause any interference, a chemical separation of the copper may be necessary before its radioactivity can be measured, since it is of course essential to count only radioactive copper. This fortunately can be checked. In general, we can say that if the half-lives and energies of artificially radioactive isotopes differ sufficiently, it is possible to determine several elements coexisting in the same sample, without chemical separation, by standard radiometric methods. More frequently, however, a chemical separation with subsequent measurement of individual components will have to be made.

If a chemical separation has to be carried out, it is first necessary to render the sample and standard into solution. The next step is to add to each solution equal and accurately weighed quantities of the element to be determined, in order that enough of the element as a whole is present to make its chemical separation relatively easy. This added element is termed the 'carrier', because it carries the artificially radioactive isotope with it, since isotopes of the same element, whether radioactive or not, possess the same chemical properties.

The carrier is always added in considerable excess compared with amount of the element actually present in the sample. The solutions are then treated in such a way that the added carrier and irradiated element are in the same chemical form; thereafter follow processes of separation needed to isolate the element, or a suitable compound of it, free from significant amounts of all other radioactive impurities. It is unnecessary that the whole of the element should be recovered during this process; knowing the amount of carrier originally added, the amount actually obtained from separation (the 'yield') can be independently determined by normal chemical analysis and proportional corrections applied for any loss of the radioactive isotope, whose mass is negligible compared with the amount of carrier added.

Either directly after irradiation or after radiochemical separation, as the case may be, the two final operations are comparisons of radioactivities of the sample and standard and confirmation that only the single required radioactivity is present.

As already indicated, the sample and standard activities are measured under identical counting conditions, while certain corrections may be necessary to ensure strict comparability of measurements. These are to allow for limitations in the counting equipment and to compensate for radioactive decay within the time interval between measurements on the sample and standard, respectively; allowance can also be made for absorption of beta-particles or gamma-rays within the specimen itself.

There are several checks to ensure that only one radioactivity is present or to ensure that 'radiochemical purity' has been attained. The first is the decay curve which shows how intensity of radioactivity falls off with time. It also indicates the time required for a given amount of radioactivity to decay to one-half of that value, *i.e.* half-life of the isotope. For neutron-irradiated copper this is 12.8 hours and the half-life is a characteristic value for any given radioactive isotope.

A second check is provided by measuring the activity with different thicknesses of aluminium sheet interposed between the sample and end-window of the Geiger-Müller tube. From a graph of the change of observed counting rate against the thickness of aluminium ('absorption curve'), maximum energy of particles or rays can be determined and compared with the known value for the radioactive isotope in question. Again, maximum energy of particles or rays from a given radio-isotope possesses a definite value.

Since the technique of radioactivation analysis was first applied in 1936 by G. von Hevesy and H. Levi¹, the greatest single factor bringing the method into prominence is undoubtedly that the slow neutron intensity, or flux, available in a nuclear reactor, such as Harwell's 'BEPO', is several hundred million times greater than the laboratory radium-beryllium neutron source used by those investigators. As sensitivity of the radioactivation method is directly dependent on the neutron flux, it is seen that extremely minute quantities of elements can be determined (*cf.* Table 28). The equipment used for the detection of radioactivity, as well as radiochemical methods of separation, have also undergone vast improvement during the last twenty years.

It is this enormous sensitivity coupled with reasonable accuracy, as well as the specific identification by half-life and energy of the particular isotope formed, which makes this such an attractive method. Another considerable advantage is a possibility of overcoming one of the troublesome analytical difficulties in normal handling of such small quantities of materials as 10^{-6} g. or less,

¹ Kgl. Danske Videnskab. Selskab, Math.-fys. Medd, 14, No. 5, 1936.

i.e. loss of the material by adsorption on vessels, precipitates, etc. In the case of radioactivation analysis, once the irradiation is completed, it is difficult to see how contamination with the element being determined could arise; as pointed out above, it is in fact common practice to add relatively large quantities of the inactive element as carrier. Once there is complete mixing between the active and inactive isotopes, problems of handling sub-microgram quantities disappear. This is the unique feature of the method.

TABLE 28
ELEMENTS DETERMINED IN TRACE QUANTITIES BY NEUTRON RADIO-ACTIVATION ANALYSIS*

<i>Elements</i>	<i>Sensitivity under ideal conditions (using Harwell Pile, BEPO)</i>
Eu, Dy	10^{-12} g
Ho, In, Ir, Lu, Mn, Re, Sm	10^{-11} to 10^{-10} g
Sb, As, Br, Cu, Ge, Au, I, La, Pd, Se, Na, Pr, Ta, Tb, Tm, W, Yb	10^{-10} to 10^{-9} g
Ba, Cd, Cs, Cl, Co, Er, Gd, Ge, Hf, Ni, Os, P, K, Rb, Sc, Y, Zn, Th, U	10^{-9} to 10^{-8} g
Ce, Cr, Hg, Mo, Sr, Te, Ti, Nd, Pt, Ru, Ag, Sn, Zr	10^{-8} to 10^{-7} g
Bi, Ca, Fe, S, Si	10^{-7} to 10^{-6} g

* This list is not exhaustive.

Radioactive isotopes of nearly all elements exist. This does not mean that activation analysis can be used to determine all these elements, since the artificially radioactive isotope must (a) be sufficiently long-lived so that it can be easily handled, transported and made ready for counting and (b) emit particles or rays of a type readily measured. It does seem, however, that determination of 70-80 elements should be possible, very light elements generally being unsuitable because of short half-life of isotopes formed and low sensitivity obtainable. Many advantages and limitations of radioactivation technique are dealt with in more detail in references listed below^{1, 2}.

APPLICATIONS TO MINERALOGY

In recent years numerous publications have appeared on determination of trace quantities of many elements in materials of chemical, chemico-legal, technological, biological, metallurgical and geological

¹ A. A. Smales, Radioactivation Analysis, *Ann. Rep. Chem. Soc.*, **46**, 1949, p. 285.

Some indications of the Scope of Radioactivation Analysis. Radioisotope Techniques, *Proc. Isotope Technique Conference*, Oxford, **2**, 1951.

The Scope of Radioactivation Analysis, *Atomics*, **4**, 1953, p. 55.

² E. N. Jenkins and A. A. Smales, *Quarterly Reviews*, **10**, 1956, p. 83.

interest, by the radioactivation method. As far as geological materials are concerned, however, it may be said that sensitivity and potentialities of the method have only recently been realized; it is quite certain that increasing use will be made of it in connexion with study of trace element distribution in all types of minerals, rocks and meteorites which, as fully appreciated in recent geological work, can contribute a vast amount of information on nature, origin and history of these materials.

A few miscellaneous examples may now be given. H. Brown and E. Goldberg¹ in U.S.A., were among the first to apply the method to materials of cosmochemical interest, by determination of traces of gallium, palladium, gold and rhenium present in some iron meteorites, which would have been practically impossible by any other technique.

In recent years, there has been an increased interest in mineral deposits containing the elements tantalum and niobium, for their use in high-temperature alloys. These two elements have close chemical similarity, so that it is relatively easy to separate the two together from other elements, but difficult to determine individual content of either tantalum or niobium alone. Tantalum may be determined by the radioactivation method, which permits determination of the tantalum content of any ore, hence also, indirectly, of the niobium content, if supplemented by straightforward chemical tests².

An activation method has also been developed for detection of traces of thorium, an element which has become important in recent years, and applied to some monazites in the presence of numerous other elements³.

Simultaneous application of autoradiography and neutron-activation has already been mentioned (p. 544), as well as the use of the latter in well-logging. Radioactive tracers and neutron-activation have also been applied in connexion with sorting of initially non-radioactive ores.

Mineral surfaces can be activated by exchange reactions with radioactive ions in solution. Furthermore, selective activation and determination of desired or undesired constituents by an (n, γ) or other type of nuclear reaction may be applied to the beneficiation of ores and coals. Activity induced by slow neutrons offers a means for concentration of many minerals. In the field of mineral-dressing, too, radioisotopes used as tracers have produced much valuable

¹ Determination of Gallium, Palladium, Gold and Rhenium in Meteorites, *Science*, **109**, 1949, p. 347; *Anal. Chem.*, **22**, 1950, p. 308.

² G. G. Eichholz, Activation Assaying for Tantalum Ores, *Nucleonics*, **10**, No. 12, 1952, p. 58.

³ E. Jenkins, Activation Analysis for Thorium, *Analyst*, **80**, 1955, p. 301.

information concerning processes used, e.g. in flotation of ores etc.^{1, 2}.

Radioactivation analyses have been carried out on traces of nickel, cobalt, and copper³. Some of these were meant to test the assertion by H. Pettersson and H. Rotschi and others, that cosmic dust constantly falling on to the earth may, in part, be the source of comparatively large amounts of nickel found in deep-sea cores, as compared with amounts found in the uppermost crust of the earth. It was considered that much pertinent information about a possible meteorite origin could be obtained from ratios nickel : cobalt, nickel : copper, copper : cobalt; hence these three elements were determined by radioactivation in representative samples of *globigerina* ooze, red clay, and marine sediments from the Atlantic, Pacific and Indian Oceans, as well as on typical examples of stony and stony-iron meteorites. Values of these ratios for the average terrestrial igneous rock were taken from the literature. A comparison of ratios for the various materials indicated that there was little contribution of meteoritic material to deep-sea sediments, unless some most remarkable differential behaviour of the three elements had taken place.

Neutron-activation analysis has been applied to determination of rubidium and caesium in the range 10^{-5} to 10^{-8} g. ⁴. Rubidium and caesium contents of North Atlantic sea-water were found to be 120 and 0.5 μ g. per litre (parts per thousand million), respectively. Additional materials of geochemical interest analysed for these elements were some marine sediment samples and a series of coals from County Durham.

Detection of minute traces of the element technetium (atomic number, 43) has recently been claimed in certain minerals rich in molybdenum and rhenium, with which technetium may be expected to be closely connected⁵.

Among many other elements of interest to the geologist may be mentioned the rare gas argon, which also illustrates one of the major limitations of the radioactivation method⁶. For purposes of absolute

¹ T. G. Church, Formation of Radioactive Surface Films on Minerals, *Canadian Journ. Research*, **28A**, 1950, p. 164.

² F. E. Senftle and A. M. Gaudin, Concentration of Ores by Induced Activities, *Nucleonics*, **8**, No. 5, 1951, p. 53.

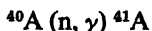
³ A. A. Smales and F. Wiseman, The Origin of Nickel in Deep-Sea Sediments, *Nature*, **175**, 1955, p. 464.

⁴ A. A. Smales and L. Salmon, Determination by Radioactivation of Small Amounts of Rubidium and Caesium in Sea-Water, and Related Materials of Geochemical Interest, *Analyst*, **80**, 1955, p. 37.

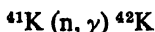
⁵ W. Herr, Occurrence of Technetium in Nature, *Z. Naturforschg.*, **9a**, 1954, p. 907.

⁶ A. A. Smales, The Scope of Radioactivation Analysis, *Atomics*, **4**, 1953, p. 55.

age determinations by the potassium-argon method, it is necessary to detect minute amounts of ^{40}Ar formed in the course of geological time in potassium minerals such as orthoclase, microcline, sylvite, etc., by slow spontaneous radioactive disintegration of the ^{40}K isotope, occurring to the extent of 0.0119% in natural potassium. The small amounts of argon may not have been sufficient to have escaped from the mineral and sensitivity of the activation method should be considerably in excess of other techniques used for argon determinations. When the argon-containing potassium mineral is irradiated in a neutron-flux, the following reaction occurs:



The ^{41}Ar is a beta- and gamma-emitter with a 1.8 hour half-life, ideal for the purpose of estimating the original argon present. However, naturally-occurring potassium in the mineral contains 6.9% of the stable ^{41}K isotope which, when irradiated with neutrons, has been shown to give the following nuclear reaction:



This is the normal type of reaction which does not interfere with the argon determination. But in addition there occurs the reaction:



meaning that a ^{41}K nucleus may absorb a neutron and emit a proton, thus yielding an ^{41}Ar nucleus. Since there is a vast excess of potassium over argon in a potassium mineral, it will be obvious that the ordinary (n, γ) reaction on ^{40}Ar to yield ^{41}Ar is 'swamped' by a much greater amount of ^{41}Ar from the (n, γ) reaction on the ^{41}K isotope present in the original sample. Such types of nuclear 'side-reactions' can occur in other cases and may or may not interfere seriously¹.

It may be possible to overcome these nuclear limitations by a partial or total separation of the element to be determined before irradiation; e.g. in the case of argon in potassium minerals, the gas may be evolved first and irradiated as such, as suggested by A. A. Smales²; in which case no interference from potassium can occur. This has been done by A. Moljk, R. W. P. Drever and S. C. Curran³ in their argon analysis of a sylvite specimen. However, such preliminary separation of minute quantities, although feasible with gases, will be very difficult for other elements at the low level which makes it necessary; in any case it is clear that much of the

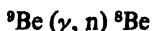
¹ A. A. Smales, *ibid.*, p. 61.

² *Ibid.*, p. 62.

³ Neutron Activation applied to Potassium Mineral Dating, *Nucleonics*, 13, No. 2, 1955, p. 44.

advantage of the radioactivation method disappears if preliminary separation is required. It may be possible to overcome the disturbing (n, p) reaction by use of a higher percentage of very slow (thermal) neutrons, which may possibly only yield a (n, γ) reaction¹.

A type of nuclear reaction in which bombardment by gamma-rays gives rise to production of neutrons, is of some importance in radioactivation analysis of many types of beryllium-containing minerals². The nuclear reaction is:



The mineral is irradiated with strong gamma-radiation from a radioactive antimony source. The neutrons formed can be counted by a standard neutron counting tube³ and a measure obtained of the amount of beryllium in the original mineral.

A method has been developed for determination of trace quantities of uranium in rocks and minerals by radioactivation analysis⁴. Natural radioactivity of these traces of uranium in various host minerals is not nearly sufficient for detection of the element by ordinary counting techniques. The object of the investigation was part of an attempt to provide methods for determining ages of individual host minerals for uranium and thorium, e.g. zircon and monazite, isolated in quite small quantities from rocks. In the past the task of treating enough rock to obtain sufficient of an individual accessory mineral for analysis by conventional methods, was sufficiently laborious to be discouraging. Uranium determinations can now be carried out on very small samples of mineral, weighing less than 0.5 g. and containing only parts per million or less of uranium. It is obvious that radioactivation technique will greatly facilitate determination of trace elements in geological material.

As a matter of interest, it may be pointed out that the activation method for uranium depends on the neutron-induced nuclear fission of some of the uranium atoms, already mentioned on p. 525. One of the fission-products produced in high yield is the radioactive isotope ¹⁴⁰Ba. This is easily separated after irradiation from the final mixture of uranium and other fission products and provides an accurate, quantitative measure of the original amount of uranium present, provided that a known amount of uranium is irradiated simultaneously to provide the usual standard.

¹ A. A. Smales, *ibid.*, p. 62.

² A. M. Gaudin and V. H. Pannell, Radioactivation Analysis of Beryllium, *Anal. Chem.*, 23, 1951, p. 1261.

³ G. B. Cook and J. F. Duncan, *Modern Radiochemical Practice*, (Clarendon Press, Oxford), 1952, p. 162.

⁴ A. A. Smales, The Determination of Small Quantities of Uranium in Rocks and Minerals by Radioactivation, *Analyst*, 77, 1952, p. 778.

APPLICATION OF MASS SPECTROMETRY TO MINERALOGY

It has already been mentioned in the introduction to this chapter that the mass spectrometer is a device for measuring the isotopic composition of any element. Almost all naturally-occurring elements consist of a mixture of isotopes and quantitative determination of this composition is becoming of increasing importance in nuclear geology and geochemistry, not only in geochronological research but also in the more general field of isotope abundance as related to geological and cosmological processes. The principle of the mass spectrometer is completely independent of radioactivity; this is fortunate, since a great majority of naturally-occurring elements is composed of mixtures of stable isotopes.

Development of the mass spectrometer for geological applications is primarily due to A. O. Nier and his associates, following upon the classic work of F. W. Aston, who first demonstrated the existence of isotopes more than three decades ago with his mass-spectrograph. It is only possible here to give a brief outline of the principles of construction of a mass spectrometer and for further information, the reader is referred to the monograph by G. P. Barnard¹.

MASS SPECTROMETER

The essentials of a mass spectrometer are shown in Fig. 88. The most important features are the ion-source, a device for producing ions of the element whose isotopic composition is to be determined; a magnetic analyser separating ions of different masses in the ion-beam; an ion-collector and electronic circuit to measure different ion-currents produced. Thus the sample whose isotopic composition is to be determined is introduced into the ion-source. When the substance to be examined is already a gas, or can be isolated from the solid sample as a gas, a small quantity of it is allowed to flow into the ion-source through a capillary tube. A beam of electrons is then fired into the vessel and effectively ionizes the gas atoms by removing other electrons from their outer orbits.

Volatile liquids, such as lead tetramethyl, can also be introduced into the ion source and behave like gases. The gas source has been used for many samples of geological interest, including examination of carbon dioxide for $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$, nitrogen for $^{15}\text{N}/^{14}\text{N}$, hydrogen for $^2\text{H}/^1\text{H}$, sulphur dioxide for $^{34}\text{S}/^{32}\text{S}$, argon for $^{40}\text{Ar}/^{36}\text{Ar}$, lead tetramethyl for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$, silicon tetrafluoride for $^{30}\text{Si}/^{28}\text{Si}$, etc.

For analysis of solid materials, e.g. lead iodide or strontium sulphate, the sample may be placed on a tungsten or platinum

¹ *Modern Mass Spectrography*, (Institute of Physics, London), 1953.

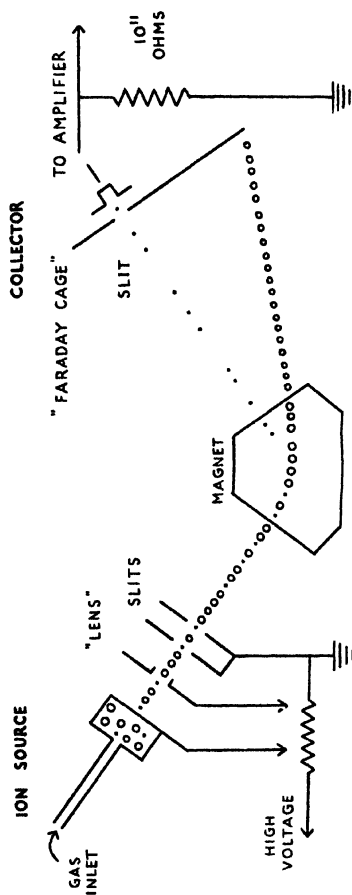


FIG. 88. Essential of a Mass Spectrometer.
(After H. Faul, *Nuclear Geology*, p. 65.)

filament which is then introduced into the source. This filament is either simply heated or an electric discharge is passed between it and another electrode. Ions of the sample become detached from the filament and can then be passed directly into the separating arrangement. It may be noted that the mass spectrometer is operated at very low pressures, so that only a minute amount of material is needed for examination. For example, samples of lead iodide, prepared from lead-containing minerals, smaller than one microgram (10^{-6} g.) have been successfully analysed isotopically for lead.

After the charged particles leave the ion-source, they pass through a series of slits in an electric field, where they are accelerated, focused and collimated. The result is that all particles of a given mass travel at the same velocity. The compound beam then passes through a magnetic field, provided by a powerful electromagnet which separates the beam into its mass constituents. Consequently particles of a particular mass accumulate at a definite point on the ion-collector.

Actually some mass spectrometers are designed so that particles of different masses are focused at different points simultaneously, while other instruments are designed so that particles of just one mass are brought to a focus at a time and particles of other masses are simply lost by collision with the walls etc.

Since the particles are electrically charged, their arrival at the ion-collector constitutes an electric current (or ion-current) which can be easily detected and measured, provided the metal ion-collector is incorporated in a suitable amplifying circuit. Considering for a moment spectrometers of the second type mentioned above, it is evident that the mass of the particles which are focused at any one time depends on the electric and magnetic fields in the separating compartment. By suitably altering these fields, particles of a second mass may be focused on to the ion-collector and further alterations will focus particles of other masses in turn. By thus allowing the electric and magnetic fields to pass through a range of values, particles of any mass may be focused and collected, one after the other.

By plotting the ion-current against the focusing field, a graph of the type shown in Fig. 89 is obtained, in which the peaks correspond to fields focusing particles whose masses are approximately multiples of the mass of the hydrogen atom. Such a graph is usually automatically traced out by an electric pen-and-ink recorder connected to the instrument and the peaks provide a measure of the isotopes present and their amounts.

In a slightly different type of mass spectrometer, two ion beams can be focused simultaneously. Such machines are used for comparing relative amounts of two isotopes in a mixture. Difference

in mass between the two isotopes can be adjusted to be one or two units and the actual masses themselves to be anywhere within a fairly wide range.

Before proceeding with some applications of the instrument, it should be emphasized that the mass spectrometer can distinguish particles only by their mass and *not* by their chemical properties. Thus, it would not be possible without a previous chemical separation to differentiate between naturally-occurring isotopes ^{50}V and ^{50}Ti , or ^{87}Rb and ^{87}Sr , etc. (except possibly by utilizing differences in ionization properties). This is a general limitation in mass spectrometric work, but it does not, however, seriously interfere in most applications. It should also be pointed out that the mass spectrometer can measure both atoms and molecules, in the latter case only if molecules are stable under these conditions.

ISOTOPE DILUTION TECHNIQUE

An extremely important application of isotope-ratio determinations lies in the highly sensitive mass spectrometric isotope dilution technique for measuring minute traces of many elements in all kinds of materials including minerals, rocks, and meteorites. This method of analysis has become a practical analytical tool with high sensitivities for many elements, largely due to the fact that separated isotopes of numerous elements are nowadays readily available from Atomic Energy laboratories. The method is a true 'sub-microgram' method and can be applied to many elements, in particular the lighter ones, for which activation analysis is unsuited.

The isotope dilution method, as used in conjunction with the mass spectrometer, can be described by outlining the general procedure and then giving a simple analytical example. The following summary of the method is taken from the work of M. G. Inghram¹. The procedure consists initially of dissolving in a suitable solvent a known weight of the sample to be analysed for a certain trace element; next is added an accurately known quantity of a separated isotope of the trace element under investigation; the resulting solution is well mixed. Since the trace element and its added isotope possess identical chemical properties, the next step is to extract the two together by a chemical method. The mixture is then examined with the mass spectrometer, which makes it possible to determine the overall change in isotopic composition of the original trace element as a result of dilution with the added isotope. Hence one can calculate the concentration of the trace element in the original sample.

¹ Trace Element Determination by the Mass Spectrometer, *Journ. Phys. Chem.*, **57**, 1953, p. 809.

Stable Isotope Dilution as an Analytical Tool, *Ann. Rev. Nuclear Sci.*, **4**, 1954, p. 81.

Fig. 94 shows a possible application of the isotope dilution method to determination of a minute amount of vanadium in, say, a mineral sample. Natural vanadium consists almost entirely of the isotope ^{51}V . To simplify matters, let us suppose that we dissolve one gram of the mineral with its unknown trace content of vanadium in a solvent, and then add one microgram (*i.e.*, 10^{-6} g. or, in this case, 1 part per million by weight) of the specially prepared ^{50}V isotope from a stock solution of known strength. After mixing,

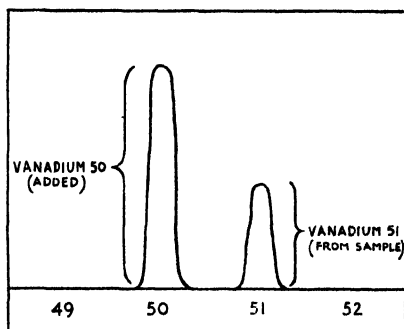


FIG. 89. Mass Spectrum of a Hypothetical Isotope Dilution Analysis of Vanadium in a Solid Sample. One ppm of vanadium⁵⁰, added as isotopic dilutant, gives the peak at mass 50. Since the peak at mass 51 is one half of this, it follows that the sample contained 0.5 ppm vanadium (as V^{51}).

some of the vanadium ($^{50}\text{V} + ^{51}\text{V}$) is chemically extracted and the resulting isotopic abundances measured mass spectrometrically. From the mass spectrum shown in the figure, we see that the ^{51}V peak (vanadium from mineral) is half the size of the ^{50}V peak (added vanadium). Since we know that there was 1 p.p.m. of the latter present, it follows that the amount of vanadium in the sample is one half of this, namely 0.5 p.p.m. Admittedly such simple cases as this seldom occur, since in general both natural and added element consist of a mixture of isotopes, each, however, of quite different proportional isotopic composition, which makes calculation of the result slightly more involved.

The main advantage of the isotope dilution method, then, is its great sensitivity and some elements such as the alkali metals can be detected and measured down to 10^{-12} to 10^{-14} g. Traces of uranium have been measured^{1, 2} in rocks and meteorites down to

¹ G. R. Tilton, C. Patterson, H. Brown, M. Inghram, R. Hayden, D. Hess, E. Larsen Jr., *Bull. Geol. Soc., Amer.*, **66**, 1955, p. 1131.

² C. Patterson, H. Brown, G. R. Tilton, M. Inghram, *Phys. Rev.*, **92**, No. 5, 1953, p. 1234.

five parts per thousand million, as shown in Fig. 90. Furthermore, with most of the suitable elements, high accuracy is possible. It is also important to note that in direct contrast to chemical methods of analysis, the final result does not depend on the quantitative chemical recovery of the element concerned. Thus, if in the above case, 80% of the ^{50}V had been lost in the chemical extraction, then 80% of the ^{51}V would also have been lost but the ratio of the two isotopes would not have altered in any way.

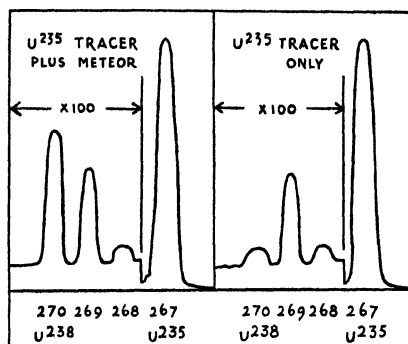


FIG. 90. Illustration of the Application of the Isotope Dilution Method to the Determination of a Trace Amount of Uranium (36). Since the ions examined are actually $(\text{UO}_2)^{++}$, the apparent mass of U^{235} is $235 + 32 = 267$. The peak at 268 and 269 are due to the oxygen isotopes O^{17} and O^{18} respectively. The change of 500% in the U^{238} abundance in the left-hand spectrum is due to the meteorite containing 5 parts per thousand million of uranium. (Terrestrial or cosmic uranium contains a great excess of U^{238} as compared to U^{235} .)

The limitation of the method is not connected with the mass spectrometry but arises from the considerable danger of contamination of the sample with traces of the element being determined, a difficulty also encountered in proportional degree in other analytical methods, though not, as explained earlier, in the activation method. At the fantastically low concentrations of trace elements to be determined, the main problems are contamination by ordinary dust from the laboratory, as well as reagent and vessel contamination during chemical processing. The latter is often taken into account by processing a blank alongside the sample, but there is no simple way of assessing the dust error. This difficulty has been partly overcome by building special dust-free laboratories for isotopic dilution work.

Another limitation of the isotope dilution method arises from the fact that samples of the element in question, having isotopic compositions considerably different from the normal, are necessary.

Some elements just do not have a second isotope suitable for use as dilutant; fortunately, however, some of these are amenable to activation analysis; the rest are available, with few exceptions, from modern Atomic Energy Isotope laboratories (Table 29).

Finally, for satisfactory operation of the mass spectrometer, a good high vacuum technique is fundamental, which introduces certain complications not met with in other analytical methods.

TABLE 29
SCOPE OF THE ISOTOPIC DILUTION METHOD¹

<i>Elements analysable</i>				<i>Elements not analysable</i>
H	V*	Pd	Gd†	F
He	Cr*	Ag*	Dy†	Na
Li*	Fe*	Cd*	Er	Al
Be	Ni*	In*	Yb	P
B*	Cu*	Sn*	Lu†	Sc
C	Zn*	Sb*	Hf	Mn
N*	Ga†	Te	W*	Co
O	Ge*	I	Re	As
Ne*	Se†	Xe*	Os	Y
Mg*	Br†	Cs	Ir	Nb
Si*	Kr*	Ba†	Pt	Rh
S†	Rb*	La†	Hg	Pr
Cl†	Sr*	Ce†	Tl	Tb
A*	Zr†	Nd†	Pb†	Ho
K†	Mo†	Pm	Th	Tm
Ca*	Tc	Sm†	U	Ta
Ti*	Ru	Eu	Pu	Au

* Isotopes immediately available in Britain².

† Isotopes expected to be available in the near future².

RECENT GEOLOGICAL APPLICATIONS OF ISOTOPE DILUTION TECHNIQUE

It is beyond the scope of this chapter to do more than mention a few of the numerous recent and interesting geological applications involving use of the isotope dilution technique; for greater detail than can be given here, suitable references are listed.

GEOCHRONOLOGY

Table 30 presents data on some mineralogical materials which were analysed for uranium by the isotope dilution method and is taken

¹ M. G. Inghram, *ibid.*, p. 812.

² Radioactive Materials and Stable Isotopes, Catalogue No. 3, July, 1954, (revised annually). Issued by Isotope Div., Atomic Energy Research Establishment, Harwell, Berks., England, *cf.* especially pp. 143-149.

from the work of H. Brown, *et al.*¹. The problem, to which most of these analyses was applied, was the geological age of different minerals occurring in a granite. The table illustrates range, sensitivity and accuracy of the method.

TABLE 30
URANIUM DETERMINATIONS BY ISOTOPE DILUTION

<i>Geological Material</i>	<i>Uranium content in parts per million</i>
Zircon	2,614 \pm 25
Sphene	299 \pm 3
Apatite	93.3 \pm 0.9
Magnetite	4.12 \pm 0.13
Perthite	0.22 \pm 0.02
Plagioclase	0.20 \pm 0.01
Quartzite	0.13 \pm 0.01
Modac stone Meteorite	0.0105 \pm 0.0003
Norton stone Meteorite	0.0054 \pm 0.0002
Ammonium Nitrate	0.000075 \pm 0.000004

The different types of age-methods in which analysis of the trace elements involved have been extensively carried out by isotope dilution techniques, together with the necessary chemical separations, are the lead-uranium, lead-thorium, potassium-argon, and rubidium-strontium methods. Many data have also been derived from determination of lead isotope ratios in lead ores and meteorites, on the possible age of the earth and of the universe. With rather few exceptions, such as the promising work on glauconite and authigenic feldspars^{2, 3}, nuclear determinations of absolute age have been made only on igneous rocks or minerals. It is not proposed to go further into the problem here, except to say that a complete summary of the principles of all present methods of age determination, together with a vast amount of actual published age data, as well as relevant references up to 1954, may be found in H. Faul's *Nuclear Geology*⁴. A much shorter review of the same topic has also been given by S. C. Curran⁵. In addition may be cited an article by H. von Ubisch⁶, concerned specifically with the application of mass spectrometry and

¹ Quoted by M. G. Inghram, *Journ. Phys. Chem.*, **57**, 1953, p. 813.

² J. I. Lipson, K-A Dating of Sediments, *Geochim. et Cosmochim. Acta*, **10**, 1956, p. 149.

³ G. J. Wasserburg, R. J. Hayden and K. T. Jensen, Dating of Igneous Rocks and Sediments, *ibid.*, p. 153.

⁴ p. 256ff.

⁵ The Determination of Geological Age by means of Radioactivity, *Quart. Rev. Chem. Soc.*, **7**, 1953, p. 1.

⁶ Mass Spectrometry and Mineralogy, *Geol. Foren. Forhandl. Stockholm*, **75**, 1953, p. 468.

isotope dilution to mineralogy, with particular reference to age determinations by the above named methods; also some work by C. H. Tomlinson and A. K. Das Gupta¹.

STABLE ISOTOPE ABUNDANCES

In the age-determinations mentioned above, isotopes measured have been formed as a result of radioactive decay through geological time. However, differences have also been found in isotopic ratios of certain other natural elements, e.g. in hydrogen, helium, carbon, boron, nitrogen, oxygen, sulphur, etc., according to conditions of their occurrence. Variations generally become less with increasing atomic weight of the element; they can be explained in part as a result of physico-chemical processes leading to slight enrichment in one isotope compared with the other and give much useful and interesting information to the geologist.

As an example, it is found that there is correlation between the temperature of sea-water and the ratio $^{18}\text{O}/^{16}\text{O}$ found in carbonate fossil shells, deposited at that temperature. A 'Palaeotemperature Scale' has been erected on this basis. Again, the proportion of the lighter isotopes of both carbon ($^{12}\text{C}/^{13}\text{C}$) and sulphur ($^{32}\text{S}/^{34}\text{S}$), appears to be higher in geological and present-day material of biological origin; in fact the earliest evidence of life on the earth may come from the isotopic ratio of carbon in rocks².

The stable isotopic abundances of a number of these lighter elements have now been determined in many types of minerals, igneous and sedimentary rocks and meteorites; excellent summaries of isotopic variation and attempts at its interpretation will be found in a number of reviews^{3, 4}.

¹ The Use of Isotope Dilution in Determination of the Geological Age of Minerals, *Canadian Journ. Chem.*, **31**, 1953, p. 909.

² K. Rankama, (i) New Evidence of the Origin of Pre-Cambrian Carbon, *Bull. Geol. Soc. Amer.*, **59**, 1948, p. 389. (ii) A Note On the Original Isotopic Composition of Terrestrial Carbon, *Journ. Geol.*, **56**, 1948, p. 199. (iii) *Corycium resuscitatum*; A discussion, *ibid.*, **58**, 1950, p. 75.

³ E. Ingerson, Non-radiogenic Isotopes in Geology: A Review, *Bull. Geol. Soc. Amer.*, **64**, 1953, p. 301.

⁴ M. L. Jensen, Geologic Importance of Variations in Stable Isotope Abundances, *Econ. Geol.*, **48**, 1953, p. 161.

CHAPTER XVI

STATISTICAL METHODS IN SEDIMENTARY PETROGRAPHY

J. C. GRIFFITHS, M.Sc., Ph.D., F.G.S.

Introduction—Frequency Distributions and their Statistical Description—Descriptive Statistics for Frequency Distributions of the Properties of Sediments—Comparison Among Sets of Data—Comparisons Among More Than Two Sets of Data—Inter-Relationships Among Variables—The Problem of Sampling Sediments—Concluding Remarks—Selected Bibliography.

INTRODUCTION¹

PROGRESS in scientific investigation in any specialized field is generally measured by the degree to which the subject is pervaded by mathematics; as expressed by J. von Neumann:

‘In modern empirical sciences it has become more and more a major criterion of success whether they have become accessible to the mathematical method or to the near-mathematical methods of physics. Indeed, throughout the natural sciences an unbroken chain of successive pseudomorphoses, all of them pressing toward mathematics, are almost identified with the idea of scientific progress, has become more and more evident’².

It seems strange therefore that, while Lyell was perhaps the earliest geologist to use statistics in establishing the Tertiary succession³, applications of mathematics to geology have since been

¹ Note. A full bibliography of authors and titles of their publications, in amplification of footnote references in the text will be found at the end of this chapter.

² The Mathematician, *The World of Mathematics*, (Simon and Schuster, New York), 1956, p. 2054.

³ R. A. Fisher, *The Expansion of Statistics*, *Journ. Roy. Stat. Soc.*, Series A, 116, 1953. See also *Amer. Sci.*, 42, 1954, p. 275. This surprisingly early example of application of statistics to a geological problem is one of the few times that geology is mentioned in textbooks or articles on statistics and their applications. A palaeontological example is cited by T. L. Kelley (*Fundamentals of Statistics*, (Harvard Univ. Press, Cambridge, Mass.), 1947), and two other examples are quoted by W. A. Wallis and H. V. Roberts (*Statistics, A New Approach*, (Free Press, Glencoe, Illinois), 1956, pp. 26–27,) under the heading of examples in the Physical Sciences.

both particulate and picaresque. Nevertheless statistical procedures, primitive and otherwise, have been fundamental in the development of geological sciences. F. W. Clarke's *Data of Geochemistry*¹ is one of the most useful statistical compilations on the 'demography' of the earth's crust and R. A. Daly's attempts to estimate volumes of different kinds of igneous rocks² are typical examples of the statistical 'problem of estimation'. It is also evident that the main shortcomings in works of this kind are lack of information on the problem of sampling, which is fundamental to all serious estimation procedures.

An entirely different and far more profound advocacy for the statistical method was proposed by T. C. Chamberlin³ in introducing 'The Method of Multiple Working Hypotheses'; indeed this is among the earliest statements in the scientific literature of the fundamentals of experimental design in problem solving.

Compare, for example, R. A. Fisher's statement⁴:

'In considering the appropriateness of any proposed experimental design it is always needful to forecast all possible results of the experiment and to have decided without ambiguity what interpretation shall be placed upon each of them.'

Again, T. C. Chamberlin⁵:

'In developing the multiple hypotheses, the effect is to bring up into view every rational explanation of the phenomenon in hand and to develop every tenable hypothesis relative to its nature, cause or origin and to give all of these as impartially as possible a working form and a due place in the investigation.'

In sedimentary petrography arguments from samples to generalizations about populations were used from the commencement and some attempts at quantitative determinations characterize the classical work of H. C. Sorby⁶, W. Mackie⁷ and J. A. Udden⁸. Indeed emphasis on grain-size analysis and, subsequently, counting frequencies of heavy minerals, led inevitably to statistical procedures for evaluation of observations and perhaps it is mostly from these two lines of endeavour that the present operational approach has arisen.

Serious overt attempts at the introduction of statistical analysis

¹ U.S.G.S., *Bull.*, 770, 1924.

² *Igneous Rocks and their Origin*, (McGraw-Hill, New York), 1914.

³ *Journ. Geol.*, 5, 1897, pp. 837-848. Reprinted, *Journ. Geol.*, 39, 1931, pp. 155-165.

⁴ *The Design of Experiments*, 6th ed., (Oliver and Boyd, London), 1951, Section 6.

⁵ *Journ. Geol.*, 39, 1931, pp. 160-161.

⁶ *Quart. Journ. Geol. Soc.*, 36, 1880, p. 46.

⁷ *Trans. Edin. Geol. Soc.*, 7, 1897, pp. 298-311.

⁸ Augustana Library Publications, 1, 1898.

commenced around 1930 (e.g. C. K. Wentworth, 1929¹; P. D. Trask, 1932²), but the main impetus sprang largely from the systematic attack, particularly on grain-size analysis, by W. C. Krumbein (1933, 1936, 1939³) and from the initial culmination of this work (W. C. Krumbein and F. J. Pettijohn, 1938⁴) most of the now varied and widespread statistical applications have since developed. The importance of statistical methods in geology has been recognized by both statisticians and geologists and a number of symposia⁵ have served to illuminate the wide and varied scope of the procedures now in use; by far the larger number of examples is drawn from the field of sedimentary petrography. A synthesis of such applications is contained in a publication by G. Herdan⁶.

Application of statistical method in any scientific investigation should commence with the formulation of the problem (see for example T. C. Chamberlin, *loc. cit.*, and R. A. Fisher, *op. cit.*) but, at least initially, the use of statistics follows upon the collection of a set of data; this is generally unfortunate, at best it usually turns out to be inefficient, at worst, completely ineffective. The collection of a set of data usually requires that the data be reduced to, and summarized in, a few statistical measures and, subsequently, several sets of data are compared and related in terms of summary statistics. Hence at the outset, statistical analysis is largely a means of presenting a succinct, comprehensible picture of a large number of data. The application of statistics in this area generally accompanies graphical portrayal of the data as frequency distributions. Following the route of historical development therefore, we commence with a review of this aspect of application of statistics to sedimentary petrography.

FREQUENCY DISTRIBUTIONS AND THEIR STATISTICAL DESCRIPTION

Any procedure leading to a set of observational data will, when

¹ *Geol. Soc. Amer., Bull.* 40, 1929, pp. 771-790.

² *Origin and Environment of Source Sediments of Petroleum*, (Gulf Publishing Co., Houston, Texas), 1932.

³ *Journ. Geol.*, 41, 1933, pp. 328-408; *Journ. Sed. Pet.*, 6, 1936, pp. 35-47; *Amer. Assoc. Petrol. Geol.*, Publication, 1939, pp. 558-591.

⁴ *Manual of Sedimentary Petrography*, (Appleton Century Crofts, New York), 1938.

⁵ The American Statistical Association formed an Earth Science Panel of their Committee on Statistics in the Physical Sciences in 1953; symposia on statistics in earth sciences were held as part of the annual meetings of the American Statistical Association in 1952 (Chicago) and 1953 (Washington). As part of the 1954 annual meeting of the Geological Society of America, W. C. Krumbein and F. Chayes organized a symposium on 'Statistical Geology' and, finally, two issues of the *Journal of Geology* (1953, 1954) were devoted to articles on 'Applied Statistics in Geology' under R. L. Miller as editor.

⁶ *Small Particle Statistics*, (Elsevier Publishing Co., New York), 1953.

repeated sufficiently often under similar conditions, generate a characteristic frequency distribution and an understanding of the form of this distribution is an essential and fundamental feature. As exigencies of space make it necessary to confine the treatment to geological aspects, it is essential that the reader should be familiar with the fundamental concepts of frequency distributions and with the various technical terms involved; and it is recommended that the relevant chapters of one or two standard works should be consulted^{1, 2, 3, 4, 5}. Nearly all the techniques and procedures for the analysis of sedimentary rocks, described in this book, generate typical frequency distributions and, fortunately, most field and laboratory analyses of rocks tend to generate well-known frequency distributions. For example, grain-size analysis of a beach sand generally tends to produce a unimodal, symmetrical frequency distribution which is characterized as log normal (W. C. Krumbein⁶, J. H. Gaddum⁷); estimates of proportions of minerals, either during thin section analysis by point-counting (F. Chayes⁸), or by counting occurrences of accessory heavy minerals, tend to generate distributions which approximate to binomial, Poisson, or hypergeometric frequency distributions (F. Chayes and H. W. Fairbairn⁹). W. C. Krumbein has summarized frequency distributions characterizing a number of techniques commonly used in petrographic analysis of sediments¹⁰. It should be emphasized that such frequency distributions are characteristic of analytical technique; change in technique generally implies change in form of the frequency distribution function.

The frequency distribution, once known, may be characterized by certain summary statistics such as the mean and variance (measures of location and dispersion), and the more complex measures of asymmetry (skewness) and peakedness (kurtosis). Many well-known distribution functions, to which observed data approximate, possess

¹ G. U. Yule and M. G. Kendall, *Introduction to the Theory of Statistics*, 14th ed., (Griffin, London), 1950.

² O. L. Davies, *Statistical Methods in Research and Production*, 3rd. ed., (Oliver and Boyd, Edinburgh), 1957.

³ C. E. Weatherburn, *A First Course in Mathematical Statistics*, 2nd ed., (Univ. Press, Cambridge), 1949.

⁴ C. A. Bennett and N. L. Franklin, *Statistical Analysis in Chemistry and the Chemical Industry*, (Wiley, New York; Chapman and Hall, London), 1954.

⁵ A. C. Aitken, *Statistical Mathematics*, 8th ed., (Oliver and Boyd, Edinburgh,) 1957.

⁶ *Journ. Sed. Pet.*, **6**, 1936, pp. 35-47.

⁷ *Nature*, **156**, 1945, pp. 463-466.

⁸ *Amer. Min.*, **31**, 1946, pp. 261-275; *Petrographic Modal Analysis* (Wiley, New York), 1956.

⁹ *Amer. Min.*, **36**, 1951, pp. 704-712.

¹⁰ *Journ. Amer. Stat. Assoc.*, **49**, 1954, pp. 51-66.

characteristic values of the summary statistics; thus the Normal or Gaussian distribution may be completely described by its mean (designated as μ) and variance (σ^2); as the normal distribution is symmetrical around the mean, its skewness is zero and its kurtosis possesses the value 3, hence there is no necessity to list the skewness and kurtosis if the frequency distribution is known to be normal. Generally however, this is not known, but suspected, and it is necessary to attempt to establish that an observed set of data represents a sample drawn from some normal population; in which case the observed statistics, based on the sample values, may be tested against those expected under the hypothesis (supposition) that the population from which the sample was drawn is normally distributed. This is one of the most useful applications of statistical analysis and may be considered a part of the process of curve fitting by means of moments. A detailed consideration of this subject is given by W. P. Elderton¹; less extended treatment is discussed in many statistical textbooks².

One of the most difficult problems in reducing frequency distributions to suitable summary statistics arises in attempting to characterize grain-size analysis of sedimentary rocks when the technique used for analysis is sieving and/or pipette sedimentation. Because sedimentary rocks are not monomineralic, but possess relatively large detrital grains of quartz, mica and fragments of other rocks together with small grains of clay minerals³, these analytical techniques generate frequency distributions characterized by 'open ends'; such frequency distributions cannot be suitably defined by moment measures (such as mean, variance, skewness and kurtosis) and many alternative descriptive measures have been proposed to overcome this difficulty⁴.

There appear to be three main lines of approach. First, it is possible to use quartile statistics⁵; secondly special statistics may be devised applying solely to these particular frequency distributions⁶; or thirdly, by changing the technique, a frequency distribution which

¹ *Frequency Curves and Correlation*, 4th ed., (Univ. Press, Cambridge), 1953.

² J. C. Smith and A. J. Duncan, *Sampling Statistics and Applications*, (McGraw-Hill, New York), 1945; also W. J. Dixon and F. J. Massey, *Introduction to Statistical Analysis*, (McGraw-Hill, New York), 1951.

³ P. D. Krynine, *Journ. Geol.*, **56**, 1948, pp. 130-165; also F. J. Pettijohn, *Sedimentary Rocks*, (Harper, New York), 1957.

⁴ W. C. Krumbein, *Amer. Assoc. Pet. Geol.*, Publication, 1939.

⁵ P. D. Trask, *op. cit.*; W. D. Krumbein, *Amer. Journ. Sci.*, **37**, 1936, pp. 98-111; W. C. Krumbein and F. J. Pettijohn, *op. cit.*, 1938.

⁶ H. A. Baker, *Geol. Mag.*, **57**, 1920, pp. 366-370; P. Niggli, *Schweiz. Min. u. Pet. Mitt.*, **15**, 1935, pp. 31-38; J. C. Griffiths, *Journ. Geol.*, **59**, 1951, pp. 211-243; D. L. Inman *Journ. Sed. Pet.*, **22**, 1952, pp. 125-145.

is amenable to conventional moment measure analysis may be generated¹.

Quartile statistics, more generally called 'order statistics', because they depend essentially on ranking observations in order and on selecting the characterizing statistical measure on the basis of its rank or order of occurrence in the entire set of ordered values. The median, for example, may be used in the place of the mean as a measure of central tendency; it is the middlemost member of any set of values and is not affected by extreme outlying values, thus being more stable than the arithmetic mean in 'open ended' frequency distributions. A relatively new field has evolved in statistics termed 'Non-parametric Methods'² and this development has arisen because in many applied fields the conventional approach via normal theory is not strictly applicable. It should be emphasized that non-parametric methods are so new that the bulk of the techniques and procedures exist as individual articles widely scattered through the literature on statistics and its applications; one example in the field of sedimentary petrography, the use of the Kolmogorov-Smirnov test for comparing open ended cumulative curves, has been described by R. L. Miller and E. C. Olson³. S. Siegel describes and illustrates large numbers of these tests⁴ and a bibliography on non-parametric statistics, including work up to 1953, is given by I. R. Savage⁵.

It seems likely that the 'open endedness' of grain-size frequency distributions is largely due to complexity of measurement of size, which results from nearly all indirect measuring techniques; such techniques fail to distinguish between complex mineral aggregates differing simultaneously in composition (*i.e.* proportions of different minerals), shape and size. In statistical terminology there are complex interactions among the variables composition, size and shape, and the final measure obtained is not easily interpretable⁶.

The third course, which appears to possess many theoretical advantages and is somewhat more general in its application⁷, will be briefly described and illustrated by example.

DESCRIPTIVE STATISTICS FOR FREQUENCY DISTRIBUTIONS OF THE PROPERTIES OF SEDIMENTS

The procedures involved in obtaining summary statistics from a

¹ J. C. Griffiths, *The Compass* (of Sigma Gamma Epsilon), 32, 1955, pp. 329-346.

² P. Hoel, *Introduction to Mathematical Statistics*, (Wiley, New York), 1947; W. J. Dixon and F. J. Massey, *op. cit.*, 1951.

³ *Journ. Geol.*, 63, 1955, pp. 376-387.

⁴ *Non-parametric Statistics for the Behavioral Sciences*, (McGraw-Hill, New York), 1956.

⁵ *Journ. Amer. Stat. Assoc.*, 48, 1953, pp. 844-906.

⁶ J. C. Griffiths, *Amer. Assoc. Pet. Geol. Bull.* 36, 1952, pp. 205-229; also *Abstr. Geol. Soc. Amer. Bull.*, 63, 1952, p. 1256.

⁷ J. C. Griffiths, *The Compass* (of Sigma Gamma Epsilon), 32, 1955, pp. 329-346.

set of measured data are quite general and may be illustrated by an example from a distribution which is approximately normal. The procedures involve derivation of summary statistics by methods of moments and cumulants and then testing certain of these statistics in order to decide that they are of physical significance, followed by a test of 'goodness of fit', whereby it may be decided whether the observed distribution matches some theoretical distribution.

The example chosen has, as its objective, measurement of grain-size of a typical quartzite; the data used in the example represent only a small part of original information compiled, in an attempt to decide the most efficient sampling pattern needed to detect differences in mean size among three outcrops of the Pottsville (Homewood) Quartzite.

Fifteen samples were selected at random from an outcrop consisting of ten large blocks of Homewood Quartzite from Coffin Rocks, near Renovo, central Pennsylvania. Five samples were taken from each of three blocks, the blocks being selected at random and the samples randomly selected from the blocks. Each sample was obtained by carefully chiselling some fifty grains from a single layer of the block of quartzite. The sampling pattern is typical for such a geological problem. It is described as multistage, hierarchical or nested¹. Each set of grains is a random sample of a sedimentation unit², each unit a random sample of the block, and each block a random sample of the outcrop. More detailed treatment of sampling procedures will follow; the scheme here presented has been determined by successive analyses of three outcrops and is the most efficient pattern we have so far been able to devise for detecting differences in mean grain-size among outcrop means of approximately 0.3 phi units³.

Nine observers measured four grains selected at random from the fifty (comprising a sample) mounted in a plastic rod⁴; thus there were 36 grains per sample and 15 samples, leading to 540 grains for the entire outcrop. The mounted grains were enlarged by means of a micro-projector and the images drawn on tracing paper. Measurements were performed on the traced images and for the present example comprised long 'a' axes measured in millimetres and transformed to phi units⁵. Selection of the long axis for measurement follows the operational definition given by J. C. Griffiths and M. A. Rosenfeld⁶.

These measured data are tabularly summarized in terms of frequency by number versus diameter in phi units in Table 31 and are portrayed as a frequency distribution in a histogram, in Fig. 91. To compute

¹ W. G. Cochran, *Sampling Techniques*, (Wiley, New York), 1953; W. C. Krumbein and H. A. Slack, *Bull. Geol. Soc. Amer.*, **67**, 1956, pp. 739-762.

² G. H. Otto, *Journ. Geol.*, **46**, 1938, pp. 569-582.

³ J. C. Griffiths, *Abstr. Geol. Soc. Amer. Bull.*, **66**, 1955, p. 1568.

⁴ C. W. H. Hulbe, *Journ. Sed. Pet.*, **25**, 1955, pp. 302-3.

⁵ W. C. Krumbein, *Journ. Sed. Pet.*, **8**, 1938, pp. 84-90.

⁶ The Penna. State Univ., *Min. Ind. Expt. St. Bull.*, **56**, 1950, pp. 202-236.

summary statistics, it is first necessary to find the moments of the distribution¹. This procedure is standard for all frequency distributions and may be facilitated by means of printed forms².

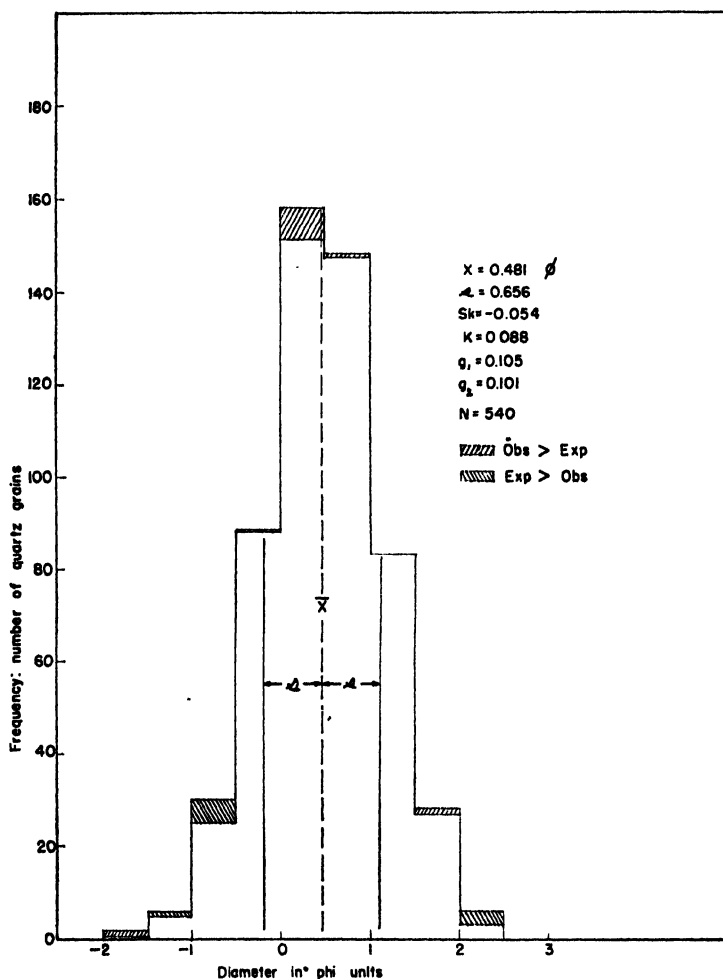


FIG. 91. Size Distribution of Quartz Grains from a Single Outcrop of Pottsville (Homewood) Quartzite, Renovo, Pennsylvania.

¹ P. Rider, *An Introduction to Statistical Method*, (Wiley, New York), 1947, p. 23; W. C. Krumbein and F. J. Pettijohn, *op. cit.*, 1938, p. 251.

² J. C. Griffiths, *The Compass* (of Sigma Gamma Epsilon), 32, 1955, pp. 329-346.

Tables of this kind may be found in most statistical texts; see for example:

P. Hoel, *op. cit.*, Table 4, p. 17.

R. Rider, *op. cit.*, Table 5, p. 23.

M. G. Kendall, *The Advanced Theory of Statistics*, 5th ed., (Griffin, London), vols. I and II, 1951/52, Table 3.1, p. 51.

W. C. Krumbein and F. J. Pettijohn, *op. cit.*, Table 29, p. 251.

J. C. Griffiths, *The Compass, etc.*, 1955, Table 2, p. 335.

In the example given by W. C. Krumbein and F. J. Pettijohn, the class interval is unity (1 phi) and hence has been omitted from all formulae for calculating the moments.

TABLE 31.

COMPUTATION OF MOMENT STATISTICS FOR THE FREQUENCY DISTRIBUTION OF LONG 'a' AXES OF 540 QUARTZ GRAINS FROM HOMEWOOD QUARTZITE

X = class mid-point; \bar{X} = arithmetic mean; \bar{X}' = assumed mean; c = class interval = 0.5 ϕ ; d = deviation = $(X - \bar{X}')/c$; f = frequency.							
Class Limits in Phi units ϕ	Frequency by Number f	Deviation d	df	d^2f	d^3f	d^4f	$(d-1)^4f$
-2.0 to -1.5	2	-4	-8	32	-128	512	1250
-1.5 to -1.0	5	-3	-15	45	-135	405	1280
-1.0 to -0.5	25	-2	-50	100	-200	400	2025
-0.5 to 0.0	88	-1	-88	88	-88	88	1408
0.0 to 0.5	158	0					158
0.5 to 1.0	148	1	148	148	148	148	0
1.0 to 1.5	83	2	166	332	664	1328	83
1.5 to 2.0	28	3	84	252	756	2268	448
2.0 to 2.5	3	4	12	48	192	768	243
Totals Σ	540	—	249	1045	1209	5917	6895

The Charlier Check, column 8, $\Sigma (d-1)^4f = \Sigma d^4f - 4 \Sigma d^3f + 6 \Sigma d^2f - 4 \Sigma df + \Sigma f$ is used as a check on the computations, e.g.:

$$6895 = 5917 - 4836 + 6270 - 996 + 540.$$

Arithmetic means of the columns (i.e., moments around the assumed mean \bar{X}'):

$$n_1 = \Sigma df / \Sigma f = 0.4611 \quad n_3 = \Sigma d^3f / \Sigma f = 2.2389$$

$$n_2 = \Sigma d^2f / \Sigma f = 1.9352 \quad n_4 = \Sigma d^4f / \Sigma f = 10.9574.$$

Moments around the estimated mean, \bar{X} ; where

$$\bar{X} = \bar{X}' + cn_1 = 0.25 + 0.5 \times 0.4611 = 0.4806.$$

First Moment (about the estimated mean) m_1 :

$$m_1 = c(n_1 - n_1) = 0.$$

Second Moment (Variance) $\sigma^2 = m_2$:

$$m_2 = c^2(n_2 - n_1^2) = 0.25 \times 1.7226 = 0.43065$$

Third Moment = m_3 :

$$\begin{aligned} m_3 &= c^3(n_3 - 3n_2n_1 + 2n_1^3) \\ &= 0.125(2.2389 - 2.6770 + 0.1960) = -0.0303. \end{aligned}$$

Fourth Moment = m_4 :

$$\begin{aligned} m_4 &= c^4(n_4 - 4n_3n_1 + 6n_2^2n_1 - 3n_1^4) \\ &= 0.0625(10.9574 - 4.1294 + 2.4685 - 0.1356) = 0.5726. \end{aligned}$$

From the moments it is customary to compute conventional measures¹ which serve to characterize the frequency distribution; a measure of skewness (Sk) is found via $\sqrt{\beta_1} = m_3/\sigma^3$, and a value of skewness sometimes taken is $Sk = 1/2\sqrt{\beta_1}$; in the present example $\sqrt{\beta_1} = 0.1072$, whence $Sk = 0.0536$. Similarly kurtosis is found as $\beta_2 = m_4/\sigma^4$ and the value of kurtosis is then $K = \beta_2 - 3$; in this case $\beta_2 = 3.0884$ and $K = +0.0884$.

R. A. Fisher has advocated the use of statistics for estimating the asymmetry (Sk) and peakedness (K) of frequency distributions, based on cumulants having some theoretical advantages over the moment measures². The cumulants for the present example are calculated in Table 32 and the 'g' statistics are derived from the cumulants in Table 33.

TABLE 32.

COMPUTATION OF THE CUMULANTS FOR THE EXAMPLE OF TABLE 31.

Cumulant $k_1 = m_1$		
„	$k_2 = (N/N-1)m_2 = 1.0019 \times 0.4306$	$= 0.4314$
„	$k_3 = [N^2/(N-1)(N-2)]m_3 = 1.0056 \times -0.0303$	$= -0.0305$
„	$k_4 = [N^2(N+1)/(N-1)(N-2)(N-3)]m_4 -$ $[3N^2/(N-2)(N-3)]m_2^2 = 1.0131$ $\times 0.5726 - 3.0280 \times 0.1854$	$= 0.0187$

¹ The β statistics and the 'g' statistics are dimensionless.

² R. A. Fisher, *Statistical Methods for Research Workers*, 12th ed., (Oliver and Boyd, Edinburgh), 1955, Section 19, App.; P. O. Johnson, *Statistical Methods in Research*, (Prentice Hall, New York,) 1949, p. 153.

TABLE 33.

CALCULATION OF FISHER'S 'g' STATISTICS FOR THE EXAMPLE OF TABLE 31

Skewness estimated by $g_1 = k_3/k_2^{3/2} = 0.1076$ Kurtosis „ „ $g_2 = k_4/k_2^2 = 0.1005$

This set of 540 observations may now be summarized in terms of four statistics, the mean (\bar{X}), the variance (s^2) and either the moment or cumulant derived estimates of asymmetry (Sk or g_1) and peakedness (K or g_2). Returning to the objective of the experiment, it is seen that these are estimates, based on this sample of 540 quartz grains, of an infinitely large population of quartz grains represented in the entire outcrop at Coffin Rocks. It is customary to regard the characteristic measures of the infinite population as *parameters* and those of the finite sample as *statistics* designated by the following notation (Table 34).

TABLE 34.

POPULATION PARAMETERS AND CORRESPONDING SAMPLE STATISTICS

Characteristic	Population	Normal Population	Samples from Populations
Mean	μ	μ	\bar{X}
Variance	σ^2	σ^2	s^2
Moment Skewness	β_1 or $\sqrt{\beta_1}$	0	$\sqrt{b_1}$
Moment Kurtosis	β_2	3	b_2
Cumulant Skewness	γ_1	0	g_1
Cumulant Kurtosis	γ_2	0	g_2

The next question is whether the sample estimates indicate that the population, of which this set of data is a random sample, is normally distributed; critical features here are asymmetry and peakedness which, in this sample of observations, appear to differ from those of a normal frequency distribution. A test is required, therefore, to decide whether these sample estimates of asymmetry and peakedness arise because the sample is so small (*i.e.* accidents of sampling or sampling error), or are indicators of real departures from normality in the population. This test of significance¹ will depend on knowing the values of the critical

¹ R. A. Fisher, *The Design of Experiments*, 6th ed., (Oliver and Boyd, Edinburgh), 1951 Sect. 7.

statistics likely to arise during random sampling of a normal population; it may be decided that if the value of asymmetry is likely to occur less than 5 times in 100 (*i.e.* less than 5 % of the time) in random sampling from a normal population, this will be regarded as evidence for rejecting the supposition of normality (similarly for the value of peakedness).

As tests of significance are standard tools in applying statistics to experimental data, the argument may be generalized as follows:

A Null Hypothesis¹ is first set up which, in this case, constitutes a statement of presupposition; this sample of 540 observations is a random sample from a normal population. Values of $\sqrt{\beta_1}$ and β_2 which will not be exceeded more than 5 times in 100 when sampling from a normal population, are tabulated against sample size² and relevant values for the present example are:

	Sample Size (N)	γ_1 ($=\sqrt{\beta_1}$)	β_2	γ_2 ($=\beta_2-3$)
From tables ²	{ 500	0.179	3.60	0.60
	{ 550	0.171	3.57	0.57
Observed Value	540	0.107	3.09	0.09

It is evident that observed values are less than those tabulated; hence, if the Null hypothesis is true, it would be expected that such values of $\sqrt{b_1}$ and b_2 would occur more often than 5 times in every 100; from the earlier decision on the level at which the hypothesis would be rejected, it may be decided that in neither case do observed values for asymmetry or peakedness contradict the hypothesis.

Similar test procedures exist for the cumulant measures³ and for large sample sizes from normal populations the values of γ_1 and γ_2 are symmetrically distributed around zero. Hence the difference between say the parametric value γ_1 and the estimated value g_1 may be tested against its standard error by the following procedures:

A statistic $t = (\gamma_1 - g_1)/s_{g_1}$ is computed where 't' is distributed as Student's 't' for infinite degrees of freedom⁴. Values of 't' for various sample sizes are tabulated in many statistic textbooks and compilations of statistical tables⁵. The test consists of computing 't' from the observations and comparing this value with those tabulated. If the observed 't'

¹ R. A. Fisher, *op. cit.*, Sect. 8.

² E. S. Pearson and H. O. Hartley, *Biometrika Tables for Statisticians*, (Univ. Press, Cambridge), I, 1954, Tables 34b, 34c, pp. 183-184.

³ It should be carefully noted that with these cumulant measures, the symbols γ_1 , γ_2 used to denote the parametric values of the estimates g_1 g_2 do not exactly correspond with the γ_1 , γ_2 used in connexion with the β coefficients.

⁴ R. A. Fisher, *Statistical Methods for Research Workers*, 12th ed., (Oliver and Boyd, Edinburgh), 1955, Sect. 23-24; P.O. Johnson, *Statistical Methods in Research*, (Prentice Hall Inc., New York), 1949, p. 155.

⁵ R. A. Fisher and F. Yates, *Statistical Tables for Biological, Agricultural and Medical Research*, 4th ed., (Oliver and Boyd, Edinburgh), 1953, Table III; H. Arkin and R. R. Colton, *Tables for Statisticians*, (Barnes and Noble, New York), 1950, Table 12, p. 116.

exceeds the value in the table for given sample size, then the hypothesis is rejected at the previously decided level of risk (= probability level).

It should be noted that this is rather a special case, since usually the degrees of freedom (and thus the significant value of t) depend upon the sample size N ; whereas here N governs the value of the standard error, which becomes larger as N decreases, while t is always taken as a normal deviate with the limiting value of 1.96 at the 5% level. It will be apparent that in small samples relatively large values of g_1 and g_2 must be reached to indicate departure from normality.

In the present example, $g_1 = 0.1076$ and the square of the standard error of g_1 is $s_{g_1}^2 = [6N(N-1)/(N-2)(N+1)(N+3)]$; $s_{g_1} = 0.1050$ and $t = g_1/s_{g_1} = 1.025$. For infinite degrees of freedom 't' at the 5% level¹ is 1.96, hence the value calculated from foregoing observations is less than the tabulated value; therefore this degree of asymmetry is expected more often than 5 times in 100 in random sampling from a normal population and constitutes no evidence for rejection of the hypothesis of normality in the parent population. Similarly a test² of g_2 suggests that the degree of peakedness observed is no larger than can be attributed to sampling error.

Tests of the 'g' statistics may be facilitated through the use of tables compiled by J. C. Griffiths and reproduced herein as Tables 35 and 36³. The computed values of g_1 and g_2 may be compared directly with the corresponding values in these tables for a specified level of risk and the required sample size and decision to reject the hypothesis of normality depends on whether or not the computed value exceeds that tabulated⁴.

Proceeding next with the original problem of estimation, it appears that departures from normality in the sample data are due to sampling error, so it may be presumed that the parent population from which this sample was drawn is effectively normal. Since large samples are required to detect departures from normality by use of moments and cumulants, a complementary and, in some cases, a more rigorous test of the hypothesis may be preferred. For this test are substituted the sample mean (\bar{X}) and variance (s^2) as population values (μ and σ^2 respectively) and the normal distribution with this mean and variance is computed.

The procedure, known as curve fitting, may be applied to compute

¹ R. A. Fisher and F. Yates, *op. cit.*, Table III.

² R. A. Fisher, *op. cit.*, 1955, p. 54; J. C. Griffiths, *op. cit.*, (*The Compass* etc.), 1955, p. 337.

³ In the original publication (see ref. 2 above), Table 6 is incorrect; the g_2 Table was reproduced in place of that for g_1 . Tests of normality using these tables are less exact than those based on tables of the β statistics listed in E. S. Pearson and H. O. Hartley (*Biometrika Tables, op. cit.*) and the error increases as sample size decreases.

⁴ W. G. Madow has added to the refinement of tests using the 'g' statistics, Note on Tests of Departures from Normality, *Journ. Amer. Stat. Assoc.*, 35, 1940, pp. 515-517.

any theoretical distribution¹; an example of its use in fitting a three term Gram-Charlier curve to an observed grain-size distribution is illustrated by G. H. Otto².

TABLE 35.

STANDARD ERROR AND SIGNIFICANCE LEVEL OF g_1 FOR DIFFERENT SAMPLE SIZES N

Sample size N	Variance $s_{g_1}^2$	Standard Error s_{g_1}	Value g_1 must exceed for significance at the level of	
			5% $t = 1.96$	1% $t = 2.58$
5000	0.001200	0.03464	0.0679	0.0894
3000	0.001998	0.04470	0.0876	0.1153
2700	0.002220	0.0471	0.0923	0.1215
2500	0.002397	0.04896	0.0960	0.1263
2000	0.002996	0.05474	0.1073	0.1412
1500	0.003992	0.06218	0.1219	0.1604
1000	0.00598	0.07733	0.1516	0.1995
900	0.006644	0.0815	0.1597	0.2103
800	0.007472	0.08644	0.1694	0.2230
700	0.008535	0.09239	0.1811	0.2384
650	0.0092	0.096	0.1882	0.2477
540	0.01103	0.105	0.2058	0.2710
500	0.01193	0.1092	0.2140	0.2817
400	0.0149	0.1220	0.2391	0.3148
300	0.01980	0.1407	0.2758	0.3630
250	0.02372	0.1540	0.3018	0.3973
200	0.02956	0.17193	0.3370	0.4436
150	0.0392	0.1980	0.3881	0.5108
100	0.05826	0.2414	0.4731	0.6228
90	0.064532	0.2540	0.4978	0.6553
80	0.072312	0.2889	0.5270	0.6938
70	0.082225	0.2868	0.5621	0.7399
60	0.095291	0.3087	0.6051	0.7964
50	0.113300	0.3366	0.6597	0.8684
40	0.139714	0.3737	0.7325	0.9641
30	0.182237	0.4268	0.8365	1.1011
25	0.215000	0.4637	0.9089	1.1963
20	0.262249	0.5121	1.0037	1.3212
15	0.336538	0.5801	1.1370	1.4967
10	0.47203	0.6870	1.3465	1.7725

¹ W. P. Elderton, *Frequency Curves and Correlation*, 4th ed., (Univ. Press, Cambridge), 1953; J. C. Smith and A. J. Duncan, *Sampling Statistics and Applications*, (McGraw-Hill, New York), 1945, p. 131 and Table 17b, p. 141; M. G. Kendall, *The Advanced Theory of Statistics*, 4th ed., (Griffin, London), I and II, 1951/52, p. 297.

² *Journ. Sed. Pet.*, 9, 1939, pp. 62-76.

TABLE 36

STANDARD ERROR AND SIGNIFICANCE LEVELS OF g_s FOR DIFFERENT SAMPLE SIZES N

Sample Size N	Variance $s_{g_s}^2$	Standard Error s_{g_s}	Value g_s must exceed for significance at the level of	
			5% $t = 1.96$	1% $t = 2.58$
5000	0.004795	0.06825	0.1338	0.1761
3000	0.007987	0.08937	0.1752	0.2306
2700	0.0089	0.0943	0.1848	0.2433
2500	0.0096	0.0980	0.1921	0.2528
2000	0.0120	0.1095	0.2146	0.2825
1500	0.0159	0.1261	0.2472	0.3253
1000	0.0239	0.1546	0.3030	0.3989
900	0.0265	0.1628	0.3191	0.4200
800	0.0298	0.1726	0.3383	0.4453
700	0.0340	0.1844	0.3614	0.4758
650	0.0369	0.1921	0.3765	0.4956
540	0.044038	0.2099	0.4114	0.5415
500	0.0475	0.2179	0.4271	0.5622
400	0.05926	0.2434	0.4771	0.6280
300	0.0787	0.2805	0.5498	0.7237
250	0.094133	0.3068	0.6013	0.7915
200	0.1171	0.3322	0.6511	0.8571
150	0.154990	0.3937	0.7715	1.0154
100	0.2288	0.4783	0.9375	1.2340
90	0.252945	0.5029	0.9857	1.2975
80	0.282796	0.5318	1.0423	1.3720
70	0.320656	0.5663	1.1099	1.4611
60	0.370263	0.6083	1.1927	1.5699
50	0.4381	0.6519	1.2777	1.6819
40	0.536703	0.7326	1.4359	1.8901
30	0.6935	0.8328	1.6323	2.1486
25	0.8131	0.9071	1.7673	2.3265
20	0.98482	0.99237	1.9450	2.5603
15	1.25641	1.120896	2.1970	2.8919
10	1.78020	1.33424	2.6151	3.4423

In the present example it comprises first reducing the normal frequency distribution, expressed as follows:

$$y = \frac{1}{\sigma \sqrt{2\pi}} e^{-x^2/2\sigma^2} \quad (1)$$

to the standard form

$$y = \frac{1}{\sqrt{2\pi}} e^{-(t^2/2)} \quad (2)$$

by transformation¹ $t = (X - \mu)/\sigma$ or equivalently by reducing the mean to zero and the standard deviation to unity. This is performed in Table 37, Columns 1 and 2. The area of the normal curve lying between these standardized class intervals is read from tables² and recorded in column 3. Since the area of the standardized normal curve is unity, the frequencies of column 4 are multiplied by $N = 540$, the area of observed frequency distribution³. Thus is obtained in Table 37, column 5, the frequency distribution expected (E) on the basis of hypotheses of normality; this may be compared with frequencies observed (O , column 6). In obtaining the expected values, certain restrictions are applied, namely that the mean, variance and area of the hypothetical curve equal that of the observed.

The deviations of the expected from the observed ($O-E$) for each class-interval are next calculated and expressed in the form of sums of squares in column 9, namely $\sum (O-E)^2/E$. These sums of squares of normal deviates may in turn be summed up to yield a value which is distributed as chi-square (χ^2), with degrees of freedom equal to the number of classes (c) compared, minus the number of restrictions (r) applied (i.e. $c-r = 8-3 = 5$). Selecting once again the level of risk (= probability) at 5%, it is found from the tabulated values of chi-square⁴ that for 5 degrees of freedom $\chi^2 = 11.070$; actually our computed value $\chi^2 = 2.41$ occurs between the 80 and 70% values in the chi-square table. In other words, on the basis of the hypothesis that this set of 540 values is a random sample from some normally distributed parent population, there is obtained on average, comparing observed with expected distributions, a value of chi-square as large as this between 70 and 80 times in every 100 trials⁵. Hence the same conclusion is reached as that from testing the moment and cumulant statistics, i.e. there is no evidence against the hypothesis of a normally distributed parent population.

On the basis of this evidence it may be claimed with some confidence that the sample values of skewness and kurtosis are results of sampling error and may be ignored in estimating grain-size population parameters of the long 'a' axes of quartz grains from this outcrop of Homewood Quartzite. The sample value of the mean is thus an estimator of the population mean and the variance is similarly an estimator of the population variance.

Limits may now be set up for these statistics which will indicate the

¹ This 't' function is quite distinct from the more familiar Student's 't'.

² E. S. Pearson and H. O. Hartley, *Biometrika Tables for Statisticians*, (Univ. Press, Cambridge), 1, 1954, Table I, p. 104; H. Arkin and R. R. Colton, *Tables for Statisticians*, (Barnes and Noble, College Outline Series, New York), 1950, Table 10, p. 114.

³ The computed frequency distribution is inserted in Fig. 91, and discrepancies between expected and observed may be examined class-interval by class-interval.

⁴ H. Arkin and R. R. Colton, *op. cit.*, Table 14, p. 121.

⁵ For fuller details concerning the χ^2 test, the textbooks of G. U. Yule and M. G. Kendall, C. E. Weatherburn, O. L. Davies, or F. A. Bennett and N. L. Franklin (see p. 568) should be consulted.

TABLE 37
THE CHI SQUARE TEST FOR GOODNESS OF FIT OF NORMAL AND OBSERVED DISTRIBUTION

$\mu = 0.4806 \quad \sigma = 0.6562$										$N = 540$	
Class	1 x $(X - \mu)$	2 x σ	3 Area (t)	4 Diff.*	5 E $N \times \text{diff.}$	6 O Obs.	7 $O - E$	8 $(O - E)^2$	9 $\frac{(O - E)^2}{E}$		
-2.0 to -1.5	-1.9806	-3.018	.998728	.001272	0.69	2	0.50	0.25	0.04		
-1.5 to -1.0	-1.4806	-2.256	.987964	.010764	5.81	5					
-1.0 to -0.5	-0.9806	-1.494	.932410	.055554	30.00	25	-5.00	25.00	0.83		
-0.5 to 0.0	-0.4806	-0.732	.767914	.164496	88.83	88	-0.83	0.69	0.01		
0.0 to 0.5	+0.0194	+0.030	.511967	.279881	151.14	158	+6.86	47.06	0.31		
0.5 to 1.0	+0.5194	+0.792	.785818	.273851	147.88	148	+0.12	0.0144	0.00		
1.0 to 1.5	+1.0194	+1.553	.939786	.153968	83.14	83	-0.14	0.02	0.00		
1.5 to 2.0	+1.5194	+2.315	.989693	.049907	26.95	28	+1.05	1.10	0.04		
2.0 to 2.5	+2.0194	+3.077	.998954	.010307	5.57	3	-2.57	6.60	1.18		
Total				1.0000	540.01	540	0.00			$\chi^2 = 2.41$	

Degrees of freedom for $\chi^2 = \text{no. of classes} - \text{no. of restrictions} = 8 - 3 = 5$.

* Column 4 is found from column 3 by difference; i.e. $1 - 0.998728 = 0.001272$; $0.998728 - 0.987964 = 0.010764$, etc.
Note around the centre of the distribution $0.279881 = (0.767914 - 0.5) + (0.511967 - 0.5)$.

degree of precision with which the corresponding parameters are estimated; for this purpose the standard error of the mean must be found¹. Thus, variance of means of samples of 540 items may be defined as:

$$s_{\bar{x}}^2 = s^2/N = 0.43065/540 = 0.0007975$$

and the corresponding standard deviation or standard error of the mean is $s_{\bar{x}} = 0.0282$. Since the means of samples from a normal population with mean μ and standard deviation σ are themselves normally distributed² with mean μ and standard deviation σ/\sqrt{N} , then the mean of 95% of samples of size 540 items lies between $\bar{X} \pm 2s_{\bar{x}} = 0.4806 \pm 0.0564$. In other words, it may be concluded that 95% of the time it is correct to state that the interval between 0.5370 and 0.4242 phi units contains the population mean of the long 'a' axis of quartz grains from the outcrop of Homewood quartzite at Coffin Rocks. This conclusion may be restated by properly claiming that a sample of 540 such measurements, possessing a mean lying outside this interval, is not a random sample of this population; such a statement will be incorrect in 5 cases out of every 100.

It should be noted that there are two approaches to this problem of estimation; it is possible to reduce any set of observations to a few summary statistics and use these statistics as estimators of population parameters. No assumptions or requirements are necessary to this procedure; however, most investigations are carried out with much more in view than this and when the various measures are to be used for physical interpretation, it is necessary to know the form of the distribution function or else to assume a likely one. It is some advantage in such circumstances to have definite physical reasons for believing that the experimental situation is represented by some well-known distribution function, such as the normal distribution in the example given above, and it is believed that log (or phi) normality is typical of many grain-size distributions under the following conditions of experimental analysis:

1. The size-measure chosen is physically simple to interpret, such as, for example, an operationally defined intercept of a single homogeneous mineral constituent.
2. The sampling procedure is correctly formulated so that only a single homogeneous sedimentation unit is included within the sample; this has so far rarely been achieved in sampling sediments (see p. 604).

There is a rather important theoretical consideration that might be mentioned here, namely the so-called 'Central Limit Theorem' of Laplace. Briefly this states that the distribution of the means of samples of N observations tends rapidly towards the normal form as the sample size N increases, irrespective of the form of the parent distribution. Thus, whatever the underlying distribution, provided one works with *means* of

¹ R. A. Fisher, *op. cit.*, 1955, Section 23.

² P. Hoel, *Introduction to Mathematical Statistics*, (Wiley, New York), 1947, p. 64.

reasonably large samples, then the properties of the normal distribution can be invoked without great inaccuracy; and the various tests of significance to be discussed in the sections that follow are, in fact, based ultimately upon the normal distribution.

Measurement of grain-size in loose grain-mounts is suitable for this purpose¹. In thin section grain-size measurement, there is a tendency to develop a skew distribution due to a cut-off of the size-range imposed by technique limitations; it is impracticable to measure grain-size much below 31.2 microns (5 phi) under experimental conditions of thin section size-measurements². In using sieve and pipette sedimentation for grain-size analysis, both conditions are unfulfilled and resulting size-frequency distributions are rarely amenable to conventional statistical analysis and generally will require non-parametric methods.

Other techniques of petrographic analysis lead to different kinds of frequency distributions and in many cases experimental conditions can be used to predict the kind of frequency distributions to be expected; thus, in point-counting thin sections for estimates of proportions of mineral constituents, F. Chayes has suggested that the hypergeometric distribution may be the most suitable model³. If the traverse length is fixed at a convenient number of points, e.g. 100, and the frequency of occurrence of the constituent per traverse is approximately constant, the resulting frequency distribution is likely to approach the binomial model; on the other hand, if the sampling unit is very large compared with the frequency of occurrence and the frequency of occurrence is again approximately constant, the Poisson model is appropriate.

By way of example, suppose that a dense mount of disaggregated grains is made from a single rock sample and the number of grains in a microscope field forms the sampling unit, then frequency of occurrence of, say zircon, will be small and the total number of grains in a field may be regarded as infinitely larger and approximately similar from field to field; under such conditions, if the dense mount is uniform over the slide, then the frequency distribution of proportion of zircons per field is likely to be Poisson in form. On the other hand, when the residue is first fractionated in bromoform and the heavy mineral concentrate mounted, the frequency of zircon is likely to show a relative increase. Furthermore, the number of grains in a microscope field is a finite and relatively small number, so that zircon frequency per field is relatively large; under these conditions frequency of zircon per field is likely to be distributed according to the binomial model. Here a change in technique has increased the probability of occurrence of zircon and transformed the frequency distribution underlying occurrence of zircon from Poisson to binomial.

¹ W. D. Pye, *Journ. Sed. Pet.*, 13, 1943, pp. 85-104; C. W. Hulbe, *Journ. Sed. Pet.*, 25, 1955, pp. 302-303; J. C. Griffiths, *Abstr. Geol. Soc. Amer. Bull.*, 66, 1955, p. 1568.

² M. A. Rosenfeld, L. Jacobsen and J. C. Ferm, *Journ. Geol.*, 61, 1953, pp. 114-132; J. R. Emery and J. C. Griffiths, *Penna. State Univ. Min. Ind. Expt. Sta. Bull.*, 62, 1953, pp. 67-80.

³ F. Chayes and H. W. Fairbairn, *Amer. Min.*, 36, 1951, pp. 704-712.

There are generally well-defined physical conditions which lead to these typical frequency distributions and the conditions under which the experiment is performed should be compared with those required to generate some specific frequency distribution. It is then possible to test empirically determined distributions to decide whether they match the theoretically postulated distribution; a considerable amount of information on the appropriate summary statistics is thereby gained, which will be informative, and will also define a model against which subsequent experiments may be checked in terms of reproducibility of technique etc. Classical work by 'Student' and R. A. Fisher followed such lines in developing counting techniques in biometry¹. The characteristics leading to development of many well-known frequency distributions are described by J. C. Smith and A. J. Duncan², G. U. Yule and M. G. Kendall³, L. H. C. Tippett⁴, C. A. Bennett and N. L. Franklin⁵; specific examples of such distributions applied to problems in sedimentary petrography are given by the authors cited below⁶.

COMPARISON AMONG SETS OF DATA

The next stage in most experimental investigations is to collect two or more sets of data and attempt to compare and contrast these sets in various ways. The first such step may well be a comparison of the means of two such sets of data. For this purpose it is customary to use Student's 't' distribution which is a 'robust' test and therefore

¹ 'Student', *Biometrika*, **5**, 1907, p. 351; **12**, 1919, p. 211; **19**, 1927, p. 1511; R. A. Fisher, *op. cit.*, 1955, Section 15; R. A. Fisher, H. G. Thornton and W. A. Mackenzie, *Annals of Applied Biology*, **9**, 1922, pp. 325-359.

² *Sampling Statistics and Applications*, (McGraw-Hill, New York), Part 1, 1945.

³ *An Introduction to the Theory of Statistics*, 14th ed., (Griffin, London), 1950, Ch. 8.

⁴ *The Methods of Statistics*, 4th ed., (Williams and Norgate, London), 1952, Ch. 11.

⁵ *Statistical Analysis in Chemistry and the Chemical Industry* (Wiley, New York), 1954, Ch. 4.

⁶ G. H. Otto, *Journ. Sed. Pet.*, **9**, 1939, pp. 62-76; P. Allen, *Nature*, **156**, 1945, p. 746; *Journ. Sed. Pet.*, **15**, 3, 1945, pp. 75-83; J. H. Gaddum, *Nature*, **156**, 1945, pp. 463-466; W. C. Krumbein, *Journ. Sed. Pet.*, **8**, 1938, pp. 84-90; *Journ. Amer. Stat. Assoc.*, **49**, 1954, pp. 51-66; *Trans. Amer. Geophys. Union*, **36**, 1955, p. 1; J. M. Dalla Valle, C. Orr Jr., and H. G. Blocker, *Ind. and Eng. Chem.*, **43**, 1951, pp. 1377-1380; G. Herdan, *Small Particle Statistics*, (Elsevier, New York), 1953, Ch. 6; M. A. Rosenfeld, *Petrographic Variation in Oriskany 'Sandstone' Complex*, Penna. State Univ., 1953; M. A. Rosenfeld and J. C. Griffiths, *Amer. Journ. Sci.*, **251**, 1953, pp. 553-585; A. N. Strahler, *Journ. Geol.*, **62**, 1954, pp. 1-25; F. Chayes and H. W. Fairbairn, *Amer. Min.*, **36**, 1951, pp. 704-712; L. H. Ahrens, *Quantitative Spectrochemical Analysis of Silicates*, (Pergamon Press, London), 1954, Ch. 4; R. L. Miller and E. D. Goldberg, *Geochimica et Cosmochimica Acta*, **8**, 1955, pp. 53-62; F. Chayes, *Geochimica et Cosmochimica Acta*, **6**, 1954, pp. 114-120; H. H. Slack and W. C. Krumbein, *Amer. Geophys. Union Trans.*, **36**, 1955, pp. 460-464; W. C. Krumbein and H. H. Slack, *Bull. Geol. Soc. Amer.*, **67**, 1956, pp. 739-762.

may be applied under a wide variety of conditions. Appropriate description of the use of 'Student's t ' is contained in most statistics texts¹.

There are three modifications of procedure. The first is used when it is desired to compare the observed mean of a single sample with some expected or postulated mean value. The second is used to compare the means of two samples or groups, the numbers of observations in which may be equal or unequal; the use of equal numbers in each group not only simplifies computation but has additionally some theoretical advantages². The third is applicable when the observations in two groups can be paired by virtue of some factor that links them. An example of the third procedure will first be given and its relation to the second type discussed.

The data in Table 38 below summarize determination of porosity on 13 samples of Bradford Oil Sand from the Bradford Oil Field in Pennsylvania; the porosity was determined by saturation with two different fluids, water and kerosene; the objective of the experiment is to determine whether the porosity measured is different for the different fluids.

The experimental arrangement, *i.e.*, the fact that both liquids were tried on the same rock specimens, is utilized and the results considered as 'paired data'; the differences of Table 38, column 4, must be found. All the differences are positive in sign; if the Null hypothesis were correct and there were no difference in porosity for either liquid, it would be expected, on average, that equal numbers of positive and negative differences would ensue. A 'sign test' could therefore be used³, where positive and negative signs would follow the binomial distribution $(p+q)^n$, in this case $(\frac{1}{2}+\frac{1}{2})^{13}$; to obtain a sample of 13 positive signs would be most unlikely⁴; actually such an occurrence would be expected once in 8192 trials.

However, taking into account magnitudes of the differences, materially increases the sensitivity of the test of the Null hypothesis; it may be calculated, therefore:

$$t = (\mu - \bar{X})/s_x \quad (5)$$

¹ R. A. Fisher, *op. cit.*, 1955, Ch. 5; L. H. C. Tippett, *The Methods of Statistics*, 4th ed., (Williams and Norgate, London), 1952, p. 146; G. H. Yule and M. G. Kendall, *op. cit.*, 1950, p. 487.

² L. H. C. Tippett, *op. cit.*, p. 148.

³ R. A. Fisher, *op. cit.*, 1955, p. 122; W. J. Dixon and F. J. Massey, *Introduction to Statistical Analysis*, (McGraw-Hill, New York), 1951, p. 247.

⁴ The test is generally an approximate one and can be performed by counting the signs of the less frequent variety and comparing this value with W. J. Dixon and F. J. Massey, (*op. cit.*, Table 10, p. 324). In the present case, with sample size $N = 13$, two negative signs would be expected 5% of the time in sampling a population where $p = 1/2$; hence as this sample yields no negative signs, the hypothesis of no difference in means may be rejected.

TABLE 38

COMPARISON OF POROSITY OF BRADFORD THIRD SAND UNDER KEROSENE AND WATER SATURATIONS¹

Sample	Porosity to Kerosene	Porosity to Water	Difference Oil-Water
1	13.35	11.63	1.72
2	14.84	11.96	2.88
3	14.42	11.65	2.77
4	15.30	12.84	2.46
5	13.36	11.69	1.67
6	11.36	8.42	2.94
7	14.64	11.07	3.57
8	16.12	14.21	1.91
9	11.94	6.91	5.03
10	15.40	12.68	2.72
11	15.69	13.26	2.43
12	12.95	8.85	4.10
13	14.12	11.87	2.25
Totals = $\sum X$	183.49	147.04	36.45
\bar{X}	14.1146	11.3108	2.8038
Sum of Squares = S.S.			
= $\sum X^2 - (\sum X)^2/N$	25.2835	51.3501	11.0793
$s^2 = S.S./N-1$	2.1069	4.2792	0.923
$s =$	1.452	2.068	0.961

where t is distributed as Student's t with degrees of freedom $N-1$; μ in this case equals zero, $s_x = \sqrt{(0.923/13)} = 0.2665$, then $t = (2.8038)/0.2665 = 10.52$ with d.f. = 12. The tabulated value of t for d.f. = 12 at the 0.1% level is 4.32² and the computed value far exceeds the tabulated ' t '. Thus, the hypothesis is rejected and it is concluded that the difference is real. In other words, porosity of these samples of Bradford Sand to kerosene exceeds the porosity to water by 2.80%. To this difference may be appended its standard error $\pm 0.27\%$ and by means of ' t ', confidence limits may actually be set to the difference. Thus may be calculated:

$$X \pm ts_x = 2.8038 \pm 4.318 \times 0.2665 = 2.8038 \pm 1.1507 = 1.6531 \text{ to } 3.9545,$$

from which may be deduced that it would be wrong one time in one thousand to claim that the true mean difference in porosity lies within these limits.

¹ M. A. Rosenfeld, *Porosity*, Part II. Some Statistical Techniques Applied to Porosity Data, unpublished M.S. thesis, Dept. of Mineralogy, The Penna. State Univ., 1950, Table XII, p. 129.

² R. A. Fisher and F. Yates, *op. cit.*, 1953.

It is instructive to consider what would have happened had the data not been paired but treated as two groups containing equal numbers of observations. This form of the test would be appropriate if there had been 26 samples assigned at random to the two liquids, instead of 13 samples each of which was treated with both liquids. The difference of the two group means indicates that the porosity of the specimens to kerosene exceeds that to water by 2.80%. This difference may be indicative of a real difference or it may be an accident of sampling. Defining now the Null hypothesis as 'these two sets of data are random samples from the same normal population', it follows that the expected mean difference in the population over a long series of trials is zero and the two estimates of variance derived from the two 'unequal' sets of data are estimates of the same variance¹.

The statistic may be computed thus in the general case where N_1 and N_2 are not equal:

$$t = \frac{\bar{X}_1 - \bar{X}_2}{s_{12}} \sqrt{\frac{N_1 N_2}{N_1 + N_2}} \quad (3)$$

where the joint standard error, $s_{12} = \sqrt{\frac{s_1^2(N_1 - 1) + s_2^2(N_2 - 1)}{N_1 + N_2 - 2}}$.

Degrees of freedom = $N_1 + N_2 - 2$.

Note that $s^2(N-1) =$ the Sum of Squares, $\frac{(\sum X)^2}{N}$.

For the special case where $N_1 = N_2 = N$, the expressions reduce to:

$$s_{12} = \sqrt{[\frac{1}{2}(s_1^2 + s_2^2)]} \text{ and } t = \frac{\bar{X}_1 - \bar{X}_2}{s_{12}} \sqrt{\frac{N}{2}}. \quad (4)$$

In the example,

$$s_{12} = \sqrt{\frac{25 \cdot 2835 + 51 \cdot 3501}{13 + 13 - 2}} \text{ or } \sqrt{[\frac{1}{2}(2 \cdot 1069 + 4 \cdot 2792)]}$$

$$= 1.787.$$

$$t = \frac{14 \cdot 1146 - 11 \cdot 3108}{1.787} \sqrt{\frac{169}{26}} \quad \text{d.f.} = 24$$

$$= \frac{2.8038}{1.787} \sqrt{6.5}$$

$$= 4.00.$$

¹ It is advisable in practice to test compatibility of the variances by means of an F test (see p. 591) to ensure that this requirement is fulfilled.

Tables of the 't' distribution¹ show that for 24 degrees of freedom and at the 5% level of risk, $t = 2.06$, and the observed value exceeds that expected under the Null hypothesis. The hypothesis is therefore rejected and it is concluded that the difference is real (with a risk of one time in 20 wrongly rejecting a true hypothesis). Actually from the table of 't', it is seen that, at the 0.1% probability level, 't' for 24 degrees of freedom equals 3.745, and it may therefore be concluded that, if the hypothesis is correct, such a value of 't' would arise less often than 1 time in 1000. Presumably it is safe to reject the hypothesis.

Although the qualitative result (rejection of the hypothesis of no difference) is the same in each case, it should be carefully noted that incorporation of the arrangement leading to 'paired data' into the initial experiment, increased the value of 't' from 4.00 to 10.52, thus apparently increasing the sensitivity of the test *i.e.*, increasing the chance of rejecting the Null hypothesis. Accompanied by the increase in 't', however, is a decrease in degrees of freedom from 24 to 12; hence, it should be realized that when differences among rock samples is large, the use of the same sample for different treatments (*i.e.* pairing the experimental treatments) leads to a marked improvement in the experiment. On the other hand, if differences among the rock-samples is small, loss of degrees of freedom by using the differences among pairs would reduce the sensitivity of the experiment. In general, it has been found that samples over a few inches apart in many sedimentary rocks are sufficiently different to recommend the use of pairing².

Finally, it must be strongly emphasized that the treatment of this example by two differing forms of the t test was purely illustrative, and must not be taken to suggest that the two procedures are in any way alternative or that data should be examined by both methods to see which gives the more favourable (or desired!) result. In practice only one or the other type of procedure is correct in any given circumstances, depending entirely upon the experimental arrangement.

It may be instructive at this stage to propose a means of using the 't' statistic to decide upon the number of samples necessary to find a mean difference of a given size at a selected level of risk. Suppose the following data represent average grain-size of the quartz grains in a sedimentary rock:

$$\bar{X} = 2.5 \text{ phi}; \quad s = 0.5 \text{ phi}; \quad N = 20.$$

¹ R. A. Fisher and F. Yates, *op. cit.*, Table III; H. Arkin and R. R. Colton, *op. cit.*, Table 12, p. 116.

² P. Licastro and J. C. Griffiths, *Penna. State Univ., Min. Ind. Expt. Sta. Bull.*, 62, 1953, pp. 41-45.

It is desired to find a difference in grain-size of 0.5 phi unit, with probability of error at the 1% level; how many grains should be measured?

By definition $t = (\mu - \bar{x})/s_{\bar{x}}$, when $s_{\bar{x}} = s/\sqrt{N}$, or more conveniently, $t^2 = N(\mu - \bar{x})^2/s^2$; then it follows that

$$N = (s^2 t^2)/(\mu - \bar{x})^2 \quad (6)$$

Substitute for the values as follows¹:

$$N = \frac{(0.5)^2 \times (2.861)^2}{(0.5)^2} = 8.2$$

i.e. 9 grains should be measured. Suppose the standard deviation is now increased to 1.0 phi unit, then

$$N = \frac{(1.0)^2 \times (2.861)^2}{(0.5)^2} = 32.7$$

or 33 grain measurements are needed. This estimate, is of course, approximate as the standard deviation based on 20 grain measurements is not very reliable². However using, say, 540 grains, the estimate is considerably improved and in many cases when a rough idea of the number of measurements needed to define a difference of a given magnitude is required, it represents an adequate first approximation. An improvement in the estimation procedure has been described by W. G. Cochran and G. M. Cox³.

COMPARISONS AMONG MORE THAN TWO SETS OF DATA

It is, of course, more common in geological investigations that a number of sets of data are available and the experimenter wishes to decide whether these sets may be combined or are representative of different populations. Here design of the experiment plays an important role and a number of ingenious arrangements exist which fit specific experimental requirements⁴. The accompanying analytical procedure, known as analysis of variance, was first proposed by R. A. Fisher⁵; each analysis of variance model may be looked upon

¹ For degrees of freedom = $N-1 = 19$ at the 0.01% level, t is found from R. A. Fisher and F. Yates, *op. cit.*, Table III, whence $t = 2.861$.

² It is possible to improve this estimate by successive approximation; in the first case, using the tabulated 't' value for $N-1 = 9-1 = 8$ degrees of freedom, yields $N = [(0.5)^2(3.355)^2]/(0.5)^2 = 11.2$ or ~ 12 and again $N = [(0.5)^2(3.0106)]/(0.5)^2 = 9.1$ or ~ 10 ; repeating for $N = 10$ or 9 degrees of freedom, yields $N = 10$ again and this is therefore the better estimate.

³ *Experimental Designs*, (Wiley, New York), 1950, p. 17.

⁴ W. G. Cochran and G. M. Cox, *op. cit.*; G. W. Snedecor, *Statistical Methods*, 4th, ed., (Iowa State College Press, Ames, Iowa), 1946; C. A. Bennett and N. L. Franklin, *op. cit.*, 1954.

⁵ *op. cit.*, 1951.

as arising from a sampling pattern and as the patterns become more complex, so the models also increase in complexity and become more precise and specific in their aims. Analysis of variance is an extremely important and flexible technique and for fuller details, including methods of computation, reference should be made to standard texts^{1, 2, 3, 4}.

The simplest model is known as the completely randomized design and arises generally from multistage, nested or hierarchical sampling patterns; as these sampling patterns are extremely common in geological problems, this analysis of variance model is of very great value to the geologist.

As an example of this kind of analytical procedure may be taken an extension of the problem in grain-size analysis, described in the section on frequency distributions. The sampling pattern comprises 3 outcrops and each outcrop was sampled by 15 samples of 50 grains each and 4 grains measured from each sample. The sampling pattern is illustrated in Fig. 92.

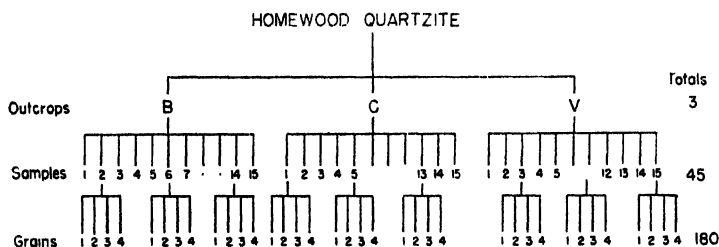


FIG. 92. Multistage Sampling Pattern for Determining Quartz Grain Size in the Homewood Quartzite, Renovo, Pennsylvania.

It should be observed that in this arrangement, grain 1 of sample 1 in outcrop B has no relationship to grain 1 of sample 1 of outcrop C and so on, which is the typical sampling plan characterized as completely randomized. Furthermore, each grain was randomly selected from the 50; and for purposes of this experiment, this may be looked upon as sampling with replacement; hence the 4 grains are a random sample of an infinite population. Similarly, the 15 samples per outcrop are random samples from an infinite population of samples at each outcrop and these three outcrops are

¹ W. G. Cochran and G. M. Cox, *op. cit.*, 1950; G. W. Snedecor, *op. cit.*, 1946.

² C. A. Bennett and N. L. Franklin, *op. cit.*, 1954.

³ K. A. Brownlee, *Industrial Experimentation*, 4th ed., (H.M.S.O., London), 1954.

⁴ M. H. Quenouille, *Introductory Statistics*, (Butterworth, London), 1950.

a random sample from a very large number of outcrops in the Homewood quartzite. This, then, is the infinite population model¹.

The computational procedure is aimed at finding the variance among grains, among sample means and outcrop means, and may be conveniently summarized in an analysis of variance (Table 39). The symbolism in this table explains how to find the mean squares (variances) which are the items to be tested in this analysis. The objective of the experiment is to attempt to find differences in quartz grain-size among outcrop means and is an experiment carried out to determine the most efficient sampling plan for analysing the grain size of the Homewood quartzite².

The first four columns of Table 39 are self-explanatory; they represent the calculation of variance (variation) which arises from the various sources. Detailed description and explanation of the steps involved may be found in references below³.

Column 5, entitled Expected Mean Square, indicates the parameters which are estimated by the Mean Squares (s^2) of column 4 and also illustrates the basis for the tests of significance associated with this kind of analysis. Here a variance ratio is used and the variabilities among sample means compared with that among grains within samples, *i.e.* the variance ratio $(\sigma_e^2 + g\sigma_m^2)/\sigma_e^2$ is formed. This procedure tests the Null hypothesis that each set of grains is a random sample from the same normal population, in which case differences among sample means will, on average, be zero, *i.e.* $\sigma_m^2 = 0$. If the hypothesis is correct, then the variance ratio $(\sigma_e^2 + g\sigma_m^2)/\sigma_e^2$ should possess the value unity. However, departures from unity may arise due to accidents of sampling and these are accounted for by the *F* distribution⁴. The procedures are best illustrated by example in performing the analysis of variance in Table 40.

¹ C. A. Bennett and N. L. Franklin, *op. cit.*, Model type II, p. 348.

² The experiment was carried out by students in a class-project in a graduate course taught by the author in the Dept. of Mineralogy at the Pennsylvania State University.

³ G. W. Snedecor, *op. cit.*, Ch. 10, p. 214; C. A. Bennett and N. L. Franklin, *op. cit.*, Ch. 7, p. 319; W. G. Cochran and G. M. Cox, *op. cit.*, Ch. 4, p. 86.

⁴ G. W. Snedecor named the distribution of the variance ratio (σ_1^2/σ_2^2) , *F* in honour of R. A. Fisher, who first proposed the use of this test in an organized manner using the 'z' distribution (see R. A. Fisher, *op. cit.*, 1955, Ch. 7). In performing such a test it is necessary to insert the largest variance in the numerator, when $s_1^2/s_2^2 = F$ follows the *F* distribution, tabulated in the references given below, with n_1 and n_2 degrees of freedom; n_1 is associated with the largest mean square s_1^2 and n_2 with s_2^2 and in general these degrees of freedom are one less than the number of items entering the computation of the respective variances. The test is performed in the usual manner and the hypothesis rejected if the *F* value found exceeds that in the table at the chosen level of risk.

G. W. Snedecor, *op. cit.*, p. 222; R. A. Fisher and F. Yates, *op. cit.*, Table V, where $F = e^{2z}$; H. Arkin and R. R. Colton, *op. cit.*, Table 13, pp. 117-120.

TABLE 39
ANALYSIS OF VARIANCE FOR THREE STAGE COMPLETELY RANDOMIZED DESIGN

Source of Variation	Degrees of Freedom	Sums of Squares (S.S.)	Mean Square	Expected Mean Square
Among Outcrops (p)	$(p-1)$	$\left[\sum_1^p \left(\sum_1^{mg} X \right)^2 / mg \right] - C.T.$	$S.S._p / (p-1)$	$\sigma_e^2 + g\sigma_m^2 + mg\sigma_p^2$
Among Samples (m) within Outcrops	$p(m-1)$	$\left[\sum_1^{pm} \left(\sum_1^g X \right)^2 / g \right] - C.T. - S.S._p$	$S.S._m / p(m-1)$	$\sigma_e^2 + g\sigma_m^2$
Among grains (g) within Samples and Outcrops	$pm(g-1)$	$S.S._{tot} - S.S._p - S.S._m$	$S.S._g / pm(g-1)$	σ_e^2
Total	$(pmg-1)$	$\sum_1^{pmg} X^2 - C.T. = S.S._{tot}$		

$$C.T. = \left(\sum_1^{pmg} X \right)^2 / pmg \quad \bar{X}_g = \left[\sum_1^{pmg} X \right] / pmg \quad C.v. \% = \frac{100 s_e}{\bar{X}_g}$$

Variation among sample means is estimated by the expected mean square $\sigma_e^2 + 4\sigma_m^2$ and this may be compared with the variation among grains σ_e^2 under the Null hypothesis that these 15 samples are all drawn from the same normal population, i.e. $\sigma_m^2 = 0$; this variance ratio yields $(s_e^2 + 4s_m^2)/s_e^2 = 8728.02/1900.60 = 4.59$, with $n_1 = 42$ degrees of freedom, and $n_2 = 135$ degrees of freedom. The tabulated value of F for 40 and 125 degrees of freedom is 1.49¹ and the value found far exceeds this; hence, this hypothesis may certainly be rejected i.e. $\sigma_m^2 \neq 0$, and there are significant differences among sample means.

TABLE 40

ANALYSIS OF VARIANCE OF QUARTZ GRAIN SIZE FROM THE HOMEWOOD QUARTZITE OF PENNSYLVANIA²

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F	F_0 from Tables ³
Among outcrops ($p = 3$)	2	66,348.63	33,348.6	3.82*	3.22
Among samples ($m = 15$)	42	366,577.07	8,728.02	4.59***	1.49
Among grains ($g = 4$)	135	256,581.25	1,900.60	—	—
Total ($pmg = 180$)	179	689,506.95	—	—	—

$$C.T. = 278,716.05 \quad \bar{X}_G = 39.35 \quad s_e = 43.595$$

$$\text{decoded } \bar{X}_G = 0.3935\phi \quad s_e = 0.4360\phi \quad \text{Cv.}\% = 110.80$$

*Asterisks are used conventionally; * significant at the 5% level; ** significant at the 1% level; *** significant at the 0.1% level.

Variation among outcrop means is similarly tested by the variance ratio $(\sigma_e^2 + 4\sigma_m^2 + 60\sigma_p^2)/(\sigma_e^2 + 4\sigma_m^2)$ and again there are significant differences among outcrop means. It should be noted that whereas the test of sample means against error (s_e^2)⁴ is significant at the 0.1%

¹ H. Arkin and R. R. Colton, *op. cit.*, p. 120.

² Data coded $X = 100$ (measured phi value).

³ R. A. Fisher and F. Yates, *op. cit.*, Table V; H. Arkin and R. R. Colton, *op. cit.*, pp. 117–120.

⁴ Where s_e^2 contains variation among grains plus all other variation arising from unassigned sources; this term is, therefore, a suitable estimate of residual, unexplained or error variation.

level¹ the test of variation among outcrop means against variation among sample means is significant at the 5% level and not significant at the 1% level. Indeed it has generally been found that to obtain significant differences among outcrop means in such a rock necessitates a well planned sampling programme with some 15 samples per outcrop; differences among sample means of sediments are generally large compared with differences among outcrop means.

The grand mean \bar{X}_G is the best estimate of the population mean, and its limits may be found as follows. The components of variance are first calculated from the actual values of the Mean Squares and the expressions for the Expected Mean Squares, and these are (in decoded units):

$$s_s^2 = 0.19006 \quad s_m^2 = 0.1707 \quad s_p^2 = 0.04103$$

The variance of a grand mean based on p outcrops, m samples and g grains is then given by the expression:

$$V(\bar{X}_G) = \frac{0.0410}{p} + \frac{0.1707}{pm} + \frac{0.19006}{pmg}$$

Putting in the actual values, $p = 3$, $m = 15$, $g = 4$,

$$V(\bar{X}_G) = 0.01846, \text{ whence } \text{s.e.}(\bar{X}_G) = 0.136.$$

The confidence interval $\bar{X}_G \pm ts_{\bar{X}_G}$ is calculated in the usual way, but care is necessary in deciding the value of t to be used in relation to the degrees of freedom. Although 180 values are involved it must be realized that the three components have been estimated with very varying degrees of accuracy. The component s_p^2 measuring variation between outcrop means is, strictly, based upon 3 samples only and is thus the least precisely estimated; yet, as will be seen from the above calculation, this component makes the largest contribution to the variance of \bar{X}_G . This uncertainty is properly allowed for if the degrees of freedom appropriate to t are taken to be those attaching to the least accurately estimated component, in this case s_p^2 ; *i.e.* 2 d.f. Thus, t is 4.30 at the 5% level, whence $ts_{\bar{X}_G} = 0.585$; and it can be stated that the true mean will be included in the interval 0.394 ± 0.585 ($= -0.191$ to 0.979) in 95 trials out of every 100.

Note that in this experiment, significant differences having been established between samples and outcrops, it would be quite incorrect to calculate the variance of the grand mean from the 'Total Variance' term and assume this to be based on 179 d.f. Such a procedure would assume that the grand mean is the mean of 180

¹ R. A. Fisher and F. Yates, *op. cit.*, Table V.

independent observations from an homogeneous set (whereas it is actually the mean of 3 outcrop means), and would seriously underestimate the variance or standard error of the grand mean! The standard error calculated on this basis would be 0.0462, or about one-third of the true value, while the use of a t value of 1.97 (for 179 d.f.) would still more seriously underestimate the breadth of the confidence interval. The use of the Total Variance for this purpose would be correct only if the whole analysis had failed to show significant differences, in which case the 180 observations could properly be regarded as coming from one population only. A confidence interval may also be calculated, called the least significant difference¹ for an outcrop mean as follows: $L.S.D._{.05} = t_{.05} s_{\bar{x}}$, where $t_{.05}$ for 42 degrees of freedom = 2.02 and $s_{\bar{x}} = \sqrt{(2M.S./k)}$.

The appropriate error mean square (E.M.S.) for comparing outcrops means, is $s_e^2 + 4s_m^2 = 8728.02$ and k equals the number of items in each mean = $mg = 60$; therefore $s_x = \sqrt{(17456.04/60)} = 17.06$, or decoded = 0.1706 and $L.S.D._{.05} = \pm 2.02 \times 0.1706 = 0.3446$; the decoded outcrop means are $\bar{X}_B = 0.2698$, $\bar{X}_C = 0.4126$, $\bar{X}_V = 0.6647$ and on the basis of the L.S.D. it can be seen that the means for outcrops B and V account for the difference².

A number of examples of application of completely randomized design to problems in sedimentary petrography are described in the literature, emphasizing that this design is eminently suited to many different kinds of geological problems³.

As our knowledge about outcome of experiments grows, it may be incorporated into the design with consequent improvement in precision of the experiment. For example, analysis of variance could be applied using randomized block design to data of Table 38 (p. 586) already examined by the t test with the following results.

This analysis makes use of the fact that each fluid was tested on the same specimen, and the total variance may be decomposed into three parts, variation among porosity means for each fluid over all samples, variation among 13 sample means over both fluids and the unassigned or error-sources of variation in Table 41. This corresponds to the use of the paired t test.

¹ L. P. V. Johnson, *An Introduction to Applied Biometrics*, (Burgess, Minnesota), 1950, p. 123.

² Many more specific tests exist for ranking means and do not require such restrictive assumptions (see R. E. Bechofer, *Ann. Math. Stat.*, **25**, 1954, pp. 16-39; R. E. Bechofer, C. W. Dunnett and M. Sobel, *Biometrika*, **41**, 1954, pp. 170-176; C. W. Dunnett, *Journ. Amer. Stat. Assoc.*, **50**, 1955, pp. 1096-1121).

³ R. L. Miller, *Journ. Palaeontology*, **23**, 1949, pp. 635-640; J. C. Griffiths, *Journ. Sed. Pet.*, **23**, 1953, pp. 75-84; J. R. Emery and J. C. Griffiths, *Penna. State Univ., Min. Ind. Expt. Sta. Bull.*, **62**, 1953, pp. 67-80; J. S. Olson and P. E. Potter, *Journ. Geol.*, **62**, 1954, pp. 26-49; P. E. Potter and J. S. Olson, *idem.*, pp. 50-73; P. E. Potter and R. Siever, *Journ. Geol.*, **63**, 1955, pp. 429-451; W. C. Krumbein and H. A. Slack, *Bull. Geol. Soc. Amer.*, **67**, 1956, pp. 739-762.

TABLE 41

ANALYSIS OF VARIANCE OF POROSITY OF BRADFORD SAND TO TWO FLUIDS:
RANDOMIZED BLOCK DESIGN

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F	Expected Mean Square
Between fluids	$(f-1) = 1$	51.10	51.10	111.18***	$\sigma_s^2 + 13\sigma_f^2$
Among samples	$(m-1) = 12$	71.09	5.92	12.8***	$\sigma_s^2 + 2\sigma_m^2$
Residual error variation	$(f-1)(m-1) = 12$	5.54	0.46	—	σ_e^2
Total	$(fm-1) = 25$	127.73	—	—	—

*** See p. 593.

There are two Null hypotheses to be tested; first, the main interest is to determine whether saturation by different fluids has any significant effect and this leads to the variance ratio $(s_s^2 + 13s_f^2)/s_s^2 = 111.18$ (compare $t = 10.52$, where $t^2 = 110.67$ of paired t test), a highly significant value; the second test of differences among sample means has a variance ratio $(s_s^2 + 2s_m^2)/s_s^2 = 12.8$, also highly significant. In effect, however, there is not a particular interest in this comparison and its rather obvious result and this arrangement has been incorporated into the experimental design merely to reduce the variation attributed to unassigned sources. This device, more generally known as blocking, is analogous to changing the sampling pattern from nested to stratified random sampling; the strata or blocks are the samples which are common to each treatment (fluid). Had each sample not been tested with both fluids, the Analysis of Variance would have taken the simpler form given in the Table 42 below, and corresponding to the group differences form of the t test.

The variance ratio, $(s_s^2 + 13s_f^2)/s_s^2 = 51.10/3.19 = 16.02$ with 1 and 24 degrees of freedom, tests the Null hypothesis that there is no significant difference between porosity means for each fluid used for saturation; the tabulated F value (for $n_1 = 1$, $n_2 = 24$) at the 0.1% level, is 14.03 indicating that observed F is highly significant and the hypothesis of no difference in mean porosity between the saturating fluids is rejected. Actually in the case where $n_1 = 1$, $F = t^2$, and so the 16.02 should compare with the $t^2 = (4.00)^2$ —(differences due to rounding error). These two analyses throw further light on the difference between the two forms of the t test, particularly in the allocation of the degrees of freedom of the residual error. And, of course, the same remarks as were made in discussing the t test apply equally here; namely, that the two analyses are given for illustrative purposes only and are not in practice alternative, the correct form depending entirely

TABLE 42

ANALYSIS OF VARIANCE OF POROSITY OF BRADFORD SAND TO TWO FLUIDS:
COMPLETELY RANDOMIZED DESIGN

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F	Expected Mean Square
Between fluids ($f=2$)	$(f-1) = 1$	51.10	51.10	16.02**	$\sigma_e^2 + 13\sigma_f^2$
Within fluids ($m = 13$)	$f(m-1) = 24$	76.63	3.19	—	σ_e^2
Total ($fm = 26$)	$(fm-1) = 25$	127.73	—	—	—

** See p. 593.

upon the original design of the experiment. It should be clear from this example that careful choice of experimental design (= arrangement of the experiment) can improve the precision or sensitivity of the experiment considerably, without increasing cost or labour involved. However, as with pairing in the 't' test, it is necessary to know beforehand that differences among samples (blocks or strata) are large enough to offset reduction in the number of degrees of freedom for error to make this change in design worthwhile. In fact, effective stratification in sampling (equivalent to effective blocking in experimental design), requires that variation within strata (blocks) is small, compared with that among strata (or blocks). For example, differences among operators performing the same experiment are generally much larger than differences within a single operator over repeated experiments; thus blocking in terms of operators may be employed to remove effects of operator differences from experimental comparisons¹. Blocking in more than one dimension may be employed for removal of more than one kind of variation from the error variance by means of such designs as Latin Squares².

In many petrographical investigations the number of samples is large and complete replication by each operator, required by such designs, is impracticable, apart from the fact that increase of block size to encompass such replication would increase variation within the

¹ J. C. Griffiths and M. A. Rosenfeld, *Penna. State Univ., Min. Ind. Expt. Sta. Bull.*, **56**, 1950, pp. 202-236; *Amer. Journ. Sci.*, **251**, 1953, pp. 192-214; *Journ. Geol.* **62**, 1954, pp. 74-91; M. A. Rosenfeld and J. C. Griffiths, *Penna. State Univ., Min. Ind. Expt. Sta. Bull.*, **56**, 1950, pp. 163-201; *Amer. Journ. Sci.*, **251**, 1953, pp. 553-585.

² F. Chayes and H. W. Fairbairn, *Amer. Min.*, **36**, 1951, pp. 704-712; W. C. Krumbein, *Journ. Sed. Pet.*, **23**, 1953, pp. 280-283; W. C. Krumbein and R. L. Miller, *Journ. Geol.*, **61**, 1953, pp. 510-532.

block until it defeats the purpose of blocking. Partial replication may then be resorted to, through the use of incomplete block designs (balanced and unbalanced incomplete block designs)¹; examples of the use of balanced square and rectangular lattices are illustrated in J. C. Griffiths, D. W. Groff and J. S. Kahn² in determining bulk density of large numbers of samples by groups of operators. Multiple or crossed classification³ may also be used for more complex experimental situations; indeed the first analysis of variance published in geological literature was a 'three cross classification'⁴ aimed at determining optimum conditions for grain size analysis by sieving⁵. A similar design was used by M. A. Rosenfeld and J. C. Griffiths⁶ to estimate effectiveness of visual determination of sphericity and roundness of quartz grains. Many more complex designs exist, such as the split-plot and factorial experiments, but they have not yet received much attention in sedimentary petrography.

It may perhaps be prudent to emphasize that use of these experimental designs, and the powerful accompanying tool of analysis of variance, carries with it certain responsibilities. First, it is advisable to select the design *before* running the experiment. Secondly, it is necessary to be specific about the questions asked, because different designs are aimed at different questions, *i.e.* different Null hypotheses and different populations. Thirdly, in most cases, the designs mentioned above can be used for two very different purposes, comparisons among means, and estimates of variance components. These two different purposes require different models, although the analysis of variance table looks similar for both and many of the arithmetical procedures are identical. C. Eisenhart⁷ has succinctly reviewed these two models and emphasized their differences. Furthermore, the populations sampled for analysis may be finite or infinite; finite populations, generally considered in Model I⁸, are used essentially to compare means, while infinite populations lead generally to estimates of variance components (Model II)⁹. Frequently a single design contains a set of 'fixed effects' from finite populations as well as samples from infinite populations leading to a mixed model (Model III)¹⁰.

¹ W. G. Cochran and G. M. Cox, *op. cit.*, Ch. 9.

² Petrographical Investigations of the Salt Wash Sediments, Prog. Rep. Mar. 1 to June 1, 1953, U.S. Atomic Energy Commission, R.M.E. 3054.

³ C. A. Bennett and N. L. Franklin, *op. cit.*, p. 385.

⁴ C. A. Bennett and N. L. Franklin, *op. cit.*

⁵ A. Swineford and F. Swineford, *Journ. Sed. Pet.*, 16, 1946, pp. 3-13.

⁶ M. A. Rosenfeld and J. C. Griffiths, *op. cit.*, 1953, pp. 553-585.

⁷ *Biometrics*, 3, 1947, pp. 1-21.

⁸ C. A. Bennett and N. L. Franklin, *op. cit.*, p. 348; W. C. Krumbein and R. L. Miller, *op. cit.*, p. 529.

^{9, 10} C. A. Bennett and N. L. Franklin, *op. cit.*

Consider an experiment in which a number of operators measure the grain-size of quartz grains from a number of rock specimens. Each operator (p) measures ' g ' grains from ' m ' specimens, the grains being randomly selected from the specimens. The sources of variation are: (1) differences among specimens over all operators; (2) differences among operators over all specimens; (3) a differential effect due to differences within one operator (called interaction or discrepancy)¹; and (4) differences among grains within operators and specimens. The model is summarized in Table 43.

It may be now assumed that it is desired to make decisions about these specimens, regarding them as a sample from an infinite population and the operators as a sample from an infinite population of operators; we use the infinite model (Model II)². On the other hand, it may be desired to make decisions about differences among these specimens and these operators, without regarding them as samples from an infinite population, but, in fact, as the entire set of specimens and operators that exist. In such a case the finite model ('fixed effects') is the correct one to use; it will be noted that the error term (σ_e^2) is used in this case to test all three effects, whereas the interaction mean square was used in the first case to test the two main effects. Finally, it may be desired to regard the operators as fixed, *i.e.* from a finite population, whereas the specimens are a small sample of an infinite population; the error variance is now used to test discrepancy and the differences among specimens, whereas the interaction mean square is used to test operator differences.

Such considerations are of paramount importance in making correct recommendations from the analysis of variance and complete grasp of these features of experimental design is necessary before attempting to use a specific arrangement for some experimental objective. Detailed treatment of these aspects are contained in C. Eisenhart³, W. G. Cochran and G. M. Cox⁴, C. A. Bennett and N. L. Franklin⁵ and many other modern statistical texts. The assumptions underlying the significance tests used in analysis of variance are also of considerable importance and implications of failure in these assumptions are described by W. G. Cochran⁶; one palliative is to transform the scale of the variate to some scale in which the assumptions are more closely approximated⁷. It may be generalized that the more clearly an experimental problem is specified, the more efficient is the analysis leading to a solution; the more rigorous the statistical method used, the more requirements must be fulfilled for the method to apply. In this respect it should be obvious that most modern refinements in method, procedure and equipment lead to greater precision in results and at the same time demand greater understanding for their proper use.

¹ G. W. Snedecor, *op. cit.*, p. 255.

² C. A. Bennett and N. L. Franklin, *op. cit.*, p. 348.

³ *Biometrics*, 3, 1947, pp. 1-21.

⁴ *op. cit.*, 1950.

⁵ *op. cit.*, 1954.

⁶ *Biometrics*, 3, 1947, pp. 22-38.

⁷ M. S. Bartlett, *Biometrics*, 3, 1947, pp. 39-57.

TABLE 43
COMPARISON OF FIXED, MIXED AND RANDOM MODELS

Source of Variation	Degrees of Freedom	Expected Mean Squares		
		Infinite Model (II)	Finite Model (I)	Mixed Model (III)
Among Specimens	$(m-1)$	$\sigma_e^2 + g\sigma_{mp}^2 + pg\sigma_m^2$	$\sigma_e^2 + pg\sigma_m^2$	$\sigma_e^2 + O + pg\sigma_m^2$
Among Operators	$(p-1)$	$\sigma_e^2 + g\sigma_{mp}^2 + mg\sigma_p^2$	$\sigma_e^2 + mg\sigma_p^2$	$\sigma_e^2 + g\sigma_{mp}^2 + mg\sigma_p^2$
Operators over Samples	$(m-1)(p-1)$	$\sigma_e^2 + g\sigma_{mp}^2$	$\sigma_e^2 + g\sigma_{mp}^2$	$\sigma_e^2 + g\sigma_{mp}^2$
Among Grains (Error)	$mp(g-1)$	σ_e^2	σ_e^2	σ_e^2
Total	$(mpg-1)$	—	—	—

INTER-RELATIONSHIPS AMONG VARIABLES

In organized research investigations it is customary to measure more than one property on the same set of specimens and generally some attempt is made to correlate the different variables and estimate the degree of association (correlation) or the form of the relationship (regression). Such inter-relationships among variables may be linear or curvilinear and simple (among a pair of variables) or multiple (among three or more variates). Proportion of accessory minerals determined by counting is related to grain-size of the sediment containing them¹; size is related to sorting in many sediments² and changes in size, shape, roundness etc. are frequently related to distance³. Analysis of these inter-relationships follows the statistical concepts of correlation and regression⁴; ultimately analysis of complex sets of data comprising measurements on, and relationships among, many variables requires multivariate analysis, a field of statistical method which permits simultaneous investigation of variation and inter-relationship among variates measured on several populations⁵.

Examples of simple linear correlations and regression are common and the requirements and assumptions necessary to the use of the method of least squares for analysis of this kind of problem are described in many statistics textbooks⁶; many examples of the application of these techniques to problems in sedimentary petrography also exist⁷.

The analysis of curvilinear relationships and multiple correlation and regression are much more complex⁸ and examples of their

¹ W. W. Rubey, *Journ. Sed. Pet.*, 3, 1933, pp. 3-29; R. Dana Russell, *Journ. Sed. Pet.*, 6, 1936, pp. 125-142; G. Rittenhouse, *Geol. Soc. Amer. Bull.*, 54, 1943, pp. 1725-1750.

² J. C. Griffiths, *Journ. Geol.*, 59, 1951, pp. 211-243.

³ F. J. Pettijohn, *Sedimentary Rocks*, (Harper, New York), 1949, pp. 395 *et seq.*

⁴ For general treatment see the textbooks of G. U. Yule and M. G. Kendall, O. L. Davies, C. E. Weatherburn, K. A. Brownlee, G. W. Snedecor, C. A. Bennett and N. L. Franklin and R. A. Fisher. Also, M. Eziakiel, *Methods of Correlation Analysis*, (Wiley, New York), 1941; M. H. Quenouille, *Associated Measurements*, (Butterworth, London), 1952.

⁵ C. R. Rao, *Advanced Statistical Methods in Biometric Research*, (Wiley, New York), 1952; M. H. Quenouille, *op. cit.*, 1952.

⁶ G. W. Snedecor, *op. cit.*, Chs. 6 and 7; R. L. Anderson and T. A. Bancroft, *Statistical Theory in Research*, (McGraw-Hill, New York), 1952, Chs. 13-16; C. A. Bennett and N. L. Franklin, *op. cit.*, Ch. 6.

⁷ W. C. Krumbein, *Journ. Geol.*, 45, 1937, pp. 577-601; 49, 1941, pp. 482-520; W. J. Plumley, *Journ. Geol.*, 56, 1948, pp. 526-577; J. C. Griffiths, *Journ. Geol.*, 59, 1951, pp. 211-243; M. A. Rosenfeld, L. Jacobsen and J. C. Ferm, *op. cit.*; G. Herdan, *Small Particle Statistics*, (Elsevier, New York), 1953; Chs. 9-12; D. H. Davis, *Journ. Geol.*, 62, 1954, pp. 102-107.

⁸ G. W. Snedecor, *op. cit.*, Chs. 13 and 14; M. Eziakiel, *op. cit.*; M. H. Quenouille, *op. cit.*

application in sedimentary petrography are rare¹. When the data, comprising two or more measured variates, are also classified, as for analysis of variance, the corresponding procedure combines analysis of variance and correlation among the variables, leading to analysis of co-variance². An example of the use of this technique in isolating the relationships among a number of variables which are inter-dependent has been described by J. S. Kahn³.

One of the most promising fields of application of statistics to sedimentary petrography concerns the exploration of the relationship between complex properties (such as porosity, permeability, viscosity, density and electrical response) and the fundamental properties of rocks (proportions of mineral constituents and their size, shape and arrangement).

For example, in attempting to elucidate the determinative rock properties which control porosity in an oil sand the following relationship was found⁴.

$$Y = 0.121X_1 + 0.129X_2 + 0.122X_3 + 0.059X_4 + 0.014X_5 - 0.415X_6 \dots (7)$$

where Y = per cent. porosity; X_1 = packing in per cent.; X_2 = phi mean grain-size; X_3 = mean per cent. of quartz; X_4 = standard deviation of axial inclination; X_5 = sorting or standard deviation in phi units; X_6 = axial ratio shape (axes b/a in millimetres).

When this is reduced to analysis of variance form as in Table 44, it is found that three of the properties account for a significant proportion of the variation in porosity and the other three properties are relatively unimportant. As the order in which these properties are arranged may alter the relative contribution of each variate, the four largest contributors, packing, shape, quartz per cent. and grain-size, were submitted to matrix analysis⁵ with the results recorded in Table 45. It is quite evident that the three main contributors are the sole contributors in

¹ Analysis of curvilinear relationships are illustrated by W. C. Krumbein, *Journ. Geol.*, **45**, 1937, pp. 557-601; W. C. Krumbein and G. D. Monk, *Trans. Amer. Inst. Min. Met. Eng.* **151**, 1943, pp. 153-163; P. Allen, *Journ. Sed. Pet.*, **17**, 1947, pp. 3-7; *Geol. Mag.*, **85**, 1948, pp. 235-241; *Quart. Journ. Geol. Soc.*, **104**, 1949, pp. 257-321; E. C. Olson and R. L. Miller, *op. cit.*; and of multiple relationships by B. H. Burma, *Journ. Palaeontology*, **23**, 1949, pp. 95-103, and R. L. Miller, *Journ. Geol.*, **62**, 1954, pp. 108-113.

² G. W. Snedecor, *op. cit.*; Ch. 12; C. A. Bennett and N. L. Franklin, *op. cit.*, Ch. 7, p. 441; W. G. Cochran and G. M. Cox, *op. cit.*, p. 74 *et seq.*

³ The Measurement of Packing in Sandstones, (Penna. State Univ.), 1954; *Journ. Geol.*, **64**, 1956, pp. 385-395.

⁴ Data from 16 samples of Berea Oil Sands (see J. R. Emery, *The Application of a Discriminant Function to a Problem in Petrology*, (Penna. State Univ.), 1954; J. R. Emery and J. C. Griffiths, Penna. State Univ., *Min. Ind. Expt. Sta. Bull.*, **62**, 1953, pp. 67-80; **64**, 1954, pp. 63-68) analysed by multiple regression procedures.

⁵ R. L. Anderson and T. A. Bancroft, *op. cit.*, p. 197; C. A. Bennett and N. L. Franklin, *op. cit.*, p. 296.

TABLE 44

ANALYSIS OF VARIANCE OF MULTIPLE REGRESSION OF POROSITY AND PETROGRAPHIC PROPERTIES OF BERE A SAND

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F
Accounted for by X_1	1	0.7647	0.7647	51.32***
Additional for X_2	1	0.0265	0.0265	1.788
„ „ X_3	1	0.1508	0.1508	10.12*
„ „ X_4	1	0.0034	0.0034	0.23
„ „ X_5	1	0.0011	0.0011	0.07
„ „ X_6	1	0.1535	0.1535	10.30*
Deviations from regression	9	0.1340	0.0149	—
Total	15	1.2340	—	—

(For degrees of freedom $n_1 = 1$ and $n_2 = 9$, $F_{.05} = 5.12$; $F_{.01} = 10.56$; $F_{.001} = 22.86$).

***, *, See p. 593.

TABLE 45

MULTIPLE REGRESSION ANALYSIS OF VARIANCE OF POROSITY AND MOST IMPORTANT PETROGRAPHIC PROPERTIES OF BERE A SAND

Source of Variation	Degrees of Freedom	Sums of Squares	Mean Square	F
Contributed by X_1	1	0.7647	0.7647	53.10***
Additional from X_2	1	0.1840	0.1840	12.78**
„ „ X_3	1	0.1268	0.1268	8.81*
„ „ X_4	1	0.0000	0.0000	—
Deviations from regression	11	0.1586	0.0144	—
Total	15	1.2340	—	—

(For d.f. $n_1 = 1$; $n_2 = 11$; $F_{.05} = 4.84$; $F_{.01} = 9.65$; $F_{.001} = 19.69$).

***, **, *, See p. 593.

this case and together they account for 87% of the variation in porosity¹. The equation expressing the relationship among these three properties and porosity may therefore be reduced to:

$$Y = 0.098X_1 - 0.327X_2 + 0.116X_3 \dots \quad (8)$$

where X_1 = packing; X_2 = grain-shape and X_3 = quartz per cent., all variates expressed in the same scales as in equation (7).

¹ Where multiple regression coefficient $R_{123}^2 = s_{123}^2/s_{tot}^2$. (see R. L. Anderson and T. A. Bancroft, *op. cit.*, p. 171) is used as a measure of the contribution of the three variables to porosity variation.

The concept of correlation, using the simple linear correlation coefficient (r), has been applied to testing grain fabric by F. Chayes¹ and by A. L. Dryden² in comparing suites of accessory heavy minerals³. An interesting discussion of some of the advantages and limitations in the use of correlation in petrography is given by F. Chayes⁴.

THE PROBLEM OF SAMPLING SEDIMENTS

Any scientific investigation is no better than its sampling plan; inadequate sampling cannot be subsequently offset by any procedure, experimental or statistical⁵ (see also Ch. II). The problem of sampling arises in the initial stages of an investigation when setting up the most efficient means of achieving the main objective of the experimental programme and it crops up again at various stages throughout the experiment in attaining required levels of precision of estimates from different measuring techniques. Because of its fundamental role in experimentation the sampling pattern should be decided upon at the same time as the overall strategy of the programme, *i.e.* at the beginning⁶; generally in sedimentary petrography it is resolved as the experimenter becomes aware of it, a certainly inefficient and, possibly, disastrous practice.

The first sampling problems to be tackled during petrographic analysis of sediments are essentially concerned with precision of estimates derived from experimental techniques. The 'probable error' approach to the estimation of precision in grain-size analysis was first described by W. C. Krumbein⁷ and an alternative approach was suggested by J. C. Griffiths⁸; G. H. Otto suggested improvements in a sample-splitter based on a comparison of sampling errors and using the theory of control⁹. Analogous treatment for accessory heavy mineral counts is discussed by A. L. Dryden¹⁰, G. Rittenhouse¹¹ and P. Allen and P. S. Walder¹². The precision or sampling error

¹ In H. W. Fairbairn, *Structural Petrology of Deformed Rocks*, (Addison Wesley Press, Mass.), 1949.

² *Amer. Journ. Sci.*, **29**, 1935, pp. 393-408.

³ See discussion of this use of ' r ' by C. Eisenhart, *Journ. Sed. Pet.*, **5**, 1935, pp. 137-145; *Amer. Journ. Sci.*, **230**, 1935, pp. 549-553; and H. Helson, *Amer. Journ. Sci.*, **232**, 1936, pp. 392-395.

⁴ *Journ. Geol.*, **57**, 1949, pp. 239-254.

⁵ W. G. Cochran, F. Mosteller and J. W. Tukey, *Amer. Stat. Assoc.*, 1954, pp. 309-331, App. G.

⁶ W. G. Cochran, F. Mosteller and J. W. Tukey, *ibid.*

⁷ *Amer. Journ. Sci.*, **27**, 1934, pp. 204-214.

⁸ *Journ. Sed. Pet.*, **23**, 1953, pp. 75-84.

⁹ *ibid.*, **7**, 1937, pp. 110-133.

¹⁰ *Proc. Nat. Acad. Sci.*, **17**, 1931, pp. 233-238.

¹¹ *Rept. Com. Sed.*, 1940, pp. 97-101, Exhibit F.

¹² *Nature*, **155**, 1945, p. 173.

associated with various aspects of preparation of heavy minerals has been evaluated by G. H. Otto¹, W. C. Krumbein and W. C. Rasmussen². Precision of thin section point count analysis and a comparison with two micrometric techniques is described by F. Chayes³ and further elaborated by F. Chayes and H. W. Fairbairn⁴. A sampling programme for thin section analysis of sediments based on 'errors' of analysis is described by J. C. Griffiths, J. A. Cochran, D. W. Groff and J. S. Kahn⁵. One of the most exhaustive surveys of precision error is contained in a co-operative project which investigated chemical, spectrochemical and petrographical techniques for the analysis of igneous rocks⁶ and various aspects of this project are discussed by W. G. Schlecht⁷, H. W. Fairbairn and J. F. Schairer⁸ and H. W. Fairbairn⁹.

Paralleling the later development in these attempts to evaluate the precision error of techniques, the 'natural variability' of sedimentary rocks has received some attention; recommendations for sampling beach sands have been made by W. C. Krumbein¹⁰ and by means of components of variance¹¹, a number of sampling programmes has been investigated to find the most efficient assignment of samples during nested or multistage sampling¹². A sampling programme designed to allow for geographical patchiness in a single 6-inch sedimentary layer together with nested sampling in terms of areas, outcrops, and localities has been proposed by P. Allen¹³.

Because correct sampling procedure is of such great importance in experimental investigations, it may be worthwhile to discuss some general rules as a guide to the sampling of sediments¹⁴. It is

¹ *Journ. Sed. Pet.*, 3, 1933, pp. 30-39.

² *ibid.*, 2, 1941, pp. 10-20.

³ *Amer. Min.*, 31, 1946, pp. 261-275; *Petrographic Model Analysis*, (Wiley, New York), 1956.

⁴ *ibid.*, 36, 1951, pp. 704-712.

⁵ *Ann. Tech. Rept.*, R.M.E. 3097, 1954, p. 25.

⁶ H. W. Fairbairn and others, *U.S. Geol. Surv. Bull.*, 980, 1951.

⁷ *U.S. Geol. Surv. Bull.*, 992, 1949, pp. 57-69; *Anal. Chem.*, 23, 1951, p. 1568.

⁸ *Amer. Min.*, 37, 1952, pp. 744-757.

⁹ *Geochimica et Cosmochimica Acta*, 4, 1953, pp. 143-156.

¹⁰ *Trans. Amer. Geophys. Union*, 34, 1953, pp. 857-868; *Proc. 4th Conf. on Coastal Eng.*, Council of Wave Research, Berkeley, Cal., 1954, Ch. 9, pp. 147-162.

¹¹ For an introductory discussion on the use of components of variance in sampling problems see: D. R. Read, *Statistical Methods with Special Reference to Analytical Chemistry*, *Roy. Inst. Chem. Monographs*, 1, 1951; C. A. Bennett and N. L. Franklin, *op. cit.*, Ch. 8, Section 3.

¹² J. S. Olson and P. E. Potter, *op. cit.*, pp. 26-49; P. E. Potter and R. Siever, *op. cit.*, pp. 429-451; W. C. Krumbein and H. A. Slack, *op. cit.*, pp. 739-762.

¹³ *Nature*, 153, 1944, p. 71; *Journ. Sed. Pet.*, 15, 3, 1945, pp. 75-83; *Quart. Journ. Geol. Soc.*, 104, 1949, pp. 257-321.

¹⁴ J. C. Griffiths, *Abstr. Geol. Soc. Amer. Bull.*, 66, 1955, p. 1568.

first necessary to realize that experiments are performed on samples to generalize the conclusions so established to the populations the samples represent. In this respect a geologist faces some very difficult problems; first there is a *hypothetical* population representing a hypothetical volume of rocks, about which the geologist wishes to draw certain conclusions. This population may be rigorously defined mathematically, but it often cannot be rigorously defined geologically, because it is difficult to decide, without equivocation, whether it was ever all deposited and some has since been removed or whether part was never deposited.

The second population may be called the *existent* population, *i.e.* that body of rock which exists at present in a certain volume of the earth's crust and this may be defined unequivocally, both statistically and geologically, but it may not be possible to sample its entirety. Hence a third population must be defined, the *available* population, which is represented by available outcrops, boreholes, road-cuts, etc. In practice even this third population is rarely sampled correctly and the geologist ends with a fourth population—the population his samples represent. A correct and efficient sampling programme should enable the geologist to apply his conclusions about the samples he describes to the available population and perhaps, as our knowledge grows, to the existent population. There will, presumably, always be some doubt about extrapolating the conclusions to the hypothetical population, except in those rare cases where this can be unequivocally defined. In many instances it will be necessary, until considerably more has been learned about sampling geological populations, to take samples at available localities and define the population which these samples represent and then, by argument, indicate that the available sampling localities lead to unbiased conclusions about the existent population. For example M. A. Rosenfeld¹ attempted to sample the Oriskany quartzite along its outcrop from northern New York State to Kentucky and the available outcrops occur on the flanks or near the tops of anticlines. The synclines are not represented, but if, as M. A. Rosenfeld argues, the thin (100–300 ft.) Oriskany did not affect the folding of the Appalachians, then the grain-size of samples at available outcrops are no different from those in the synclines etc. Hence the available samples are representative of the existent population. It will undoubtedly be necessary to test this argument in those cases where three-dimensional control of the sampling is possible, *e.g.* in areas exhaustively drilled for oil or uranium, or in areas like the Colorado Plateau, where exposures are continuous for hundreds of miles in some formations.

¹ *Petrographic Variation in Oriskany 'Sandstone' Complex*, Penna. State Univ., 1953.

Another aspect of sampling geological populations which needs emphasis is the objective of enquiry; consider the following idealized models¹. First, a source-bed and its weathered product slides by gravity down a mountain slope as talus, scree, and mudflow. The sedimentary deposit is uniformly heterogeneous (Fig. 93, stage 1). It is desired to determine the population mean size and variance by sampling the deposit. Any sample large enough to contain the largest quartz grain will be a random sample of this population and if a set of samples is taken in a grid, each sample will yield an efficient estimate of the population mean and variance. It is then found that the variance of each set of grains within a sample is large and estimates the population variance, whereas the variance among sample means is small.

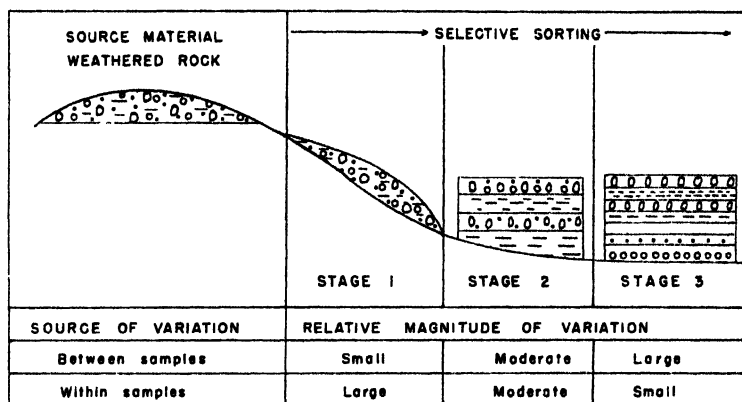


FIG. 93. Variation Among and Within Samples of Sedimentary Deposits; a basic model for defining sampling patterns.

(After Griffiths, 1955b.)

At the other extreme, if the source material travels several thousands of miles by stream transport, there is a strong selective sorting effect on the sizes of the quartz grains and the resulting deposit is layered or occurs as strata. Each sample is taken within one layer or stratum and is large enough to contain the largest quartz grain; a set of quartz grains is measured in each sample. Now the variance among grains within samples is small, but the variance among sample means is large (Fig. 93, stage 3). No single sample yields an estimate of the population mean and variance by itself.

Here obviously different sampling programmes must be used; in stage 1 many grains within each sample and few samples are

¹ J. C. Griffiths, *Abstr. Geol. Soc. Amer. Bull.*, 66, 1955, p. 1568.

needed; at stage 3 many samples are required with a few grains in each. There are, of course, intermediate cases¹ and it will be necessary, in practice, to perform a preliminary investigation to determine the most efficient sampling programme for each specific case until adequate objective criteria are obtained, enabling a decision to be made as to which programme is the most efficient.

It should be noted that to achieve an efficient estimate of the population mean and variance a channel sample across the entire deposit would serve the purpose at all stages, but a very large amount of important geological information may thereby be lost. It is not inconceivable that the mean sizes of quartz grains in many beach sands and glacial tills are similar and the population variances may also not be very different; the fundamental difference is that the till is homogeneous, whereas the beach sand is finely layered and in the distribution pattern of means and variances among and within samples lies the clue to fundamental environmental differences. Finally, it should be realized that in many cases it cannot be decided, without performing the measurements on samples, whether the population is stratified or not and channel samples are inadequate for this purpose; indeed grid samples which are so placed that they intersect several layers and/or parts of layers are equally misleading and unless it can be guaranteed that the sampling programme follows the recommendations first proposed by E. T. Apfel² and G. H. Otto³, the objective of the experimental investigation may be completely defeated⁴.

It may, then, be concluded that to achieve an adequate and efficient sampling programme it is necessary, first, to define clearly the objective of the experiment, secondly, to run a preliminary investigation leading to estimates of components of variance and, then, based on the ratios of these variances, to select a sampling plan which will 'fit' the sedimentary deposit and not defeat the objective. It seems reasonably clear that since the statistician borrowed the term stratified random sampling from the geologist⁵, some kind of stratified random sampling will generally be the most efficient programme for solving problems in sedimentary geology.

CONCLUDING REMARKS

The applications of statistical analysis in sedimentary petrography,

¹ J. R. Curray and J. C. Griffiths, *Geol. Soc. Amer. Bull.*, 66, 1955, pp. 1075-1096, and Fig. 98, stage 2.

² *Journ. Sed. Pet.*, 8, 1938, pp. 67-68.

³ *Journ. Geol.*, 46, 1938, pp. 569-582.

⁴ J. C. Griffiths, *et al.*, *Ann. Tech. Rept.*, R.M.E. 3097, 1954; *Prog. Rep.*, R.M.E. 3106, 1954; R. Steinmetz, Penna. State Univ., 1956, pp. 1-116.

⁵ W. G. Cochran, *Sampling Techniques*, (Wiley, New York), 1953.

reviewed here in brief, do not by any means exhaust the possibilities. Many quite important aspects are only incidentally mentioned, such as the use of the chi-square statistic in contingency tables¹. This procedure has a wide field of application in the study of attributes² and will therefore be of great value in analysing data generally collected during field-work. Very little use has so far been made of Rank Correlation Methods³.

The problem of assigning an interpretative implication to 'unusual' occurrences of boulders in silts and clays or coal seams, will need examination by procedures described under 'Extreme Value Theory'⁴ before an 'assignable cause' in place of 'chance occurrence' is ascribed to these rare events. In fact, since the geologist deals with long time intervals and large volumes of rock, the occurrence of occasional 'very extreme' values is to be expected.

Most problems in geology require examination of many variables, and as these variables are rarely independent or completely dependent⁵, multivariate analysis becomes a necessary procedure; as mentioned by E. C. Olson and R. L. Miller⁶, the procedure called 'Factor Analysis' evolved by L. L. Thurstone⁷ appears to be an obvious approach, which will enable many, at present obscure, problems in sedimentary geology to be approximately solved.

Time series analysis⁸ is also a fertile future field for sedimentary petrographers interested in such problems as trends with time, cycles of sedimentation etc.⁹; and as the field of statistical methodology grows and familiarity with its procedures becomes more common among geologists, it will be necessary to delve into stochastic processes and decision functions¹⁰. Indeed, it may be concluded that nearly all the developments in statistical methodology provide tools which are suitable for application to some problem in sedimentary geology.

¹ C. Eisenhart, *Amer. Journ. Sci.*, **230**, 1935, pp. 549-553.

² G. U. Yule and M. G. Kendall, *op. cit.*, Chs. 1-3.

³ M. G. Kendall, *Rank Correlation Methods*, (Griffin, London), 2nd ed. 1954; M. J. Moroney, *Facts from Figures*, (Penguin Books, London), 1951; S. Siegel, *op. cit.*

⁴ E. J. Gumbel, *Nat. Bur. Standards*, Applied Mathematics Series, **33**, 1954; W. C. Krumbein and J. Lieblein, *Trans. Amer. Geophys. Union*, **37**, 1956, pp. 313-319.

⁵ J. C. Griffiths, *Amer. Assoc. Pet. Geol. Bull.*, **36**, 2, 1952, pp. 205-229.

⁶ *Journ. Palaeontology*, **25**, 1951, pp. 212-223.

⁷ *Multiple Factor Analysis*, (Univ. of Chicago Press), 1947.

⁸ L. H. C. Tippett, *op. cit.*, 1952.

⁹ A. B. Ronov, *Bull. de l'Academie des Sciences de l'U.S.S.R.* **IX**, **4**, 1946, pp. 383-392; A. B. Vistelius, *Compt. Rend. (Doklady) Acad. Sci., U.S.S.R.*, **44**, 1944, pp. 26-30; **54**, 1945, pp. 515-517.

¹⁰ *Inst. Math. Stat.*, (McGraw-Hill, New York), 1955.

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